INTERIM REPORT

EFFECTS OF ACID PRECIPITATION ON NED PROJECTS

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ABSTRACT

No dramatic effects from acid precipitation on NED projects were noted in this report. However, levels of alkalinity at some projects are extremely low indicating minimal resistance to further watershed acidification, and aluminum levels are near, and in some cases above, the levels that have been found toxic at other sites by some researchers. Further research needs to be done on improving the quality of the data collected by NED's automatic water quality monitors and on determining the forms of aluminum in the waters of NED projects.

This report is an update to the "Interim Report, Effects of Acid Precipitation on NED Projects" dated November 1984. In the four years since that report was produced, Barre Falls, Birch Hill, and Franklin Falls Dams, and North Hartland Lake have been added to the study and Union Village Dam was dropped bringing the total number of projects to ten. Automatic water quality monitor plots for these projects from 1982 through 1987 are included in this update. NED has also begun collecting precipitation quality data at some projects and has gathered a large amount of precipitation quality data from other researchers.

Using precipitation data from all available sources, a method was developed for combining these data and plotting total acid load throughout the year. Because time did not permit plotting these data for all ten projects, three representative projects on a North-South axis were chosen: Franklin Falls Dam, Tully Lake, and Thomaston Dam. These plots show that the acid load tends to be greatest during the summer, and that there is no obvious relationship between pH levels in the runoff and specific acid loading events. A literature review shows that no simple relationship between acid load in storms and pH in the runoff should be expected.

A review of the literature shows that no good criterion to protect sensitive aquatic life from hazardous levels of aluminum have yet been developed. This is in part because of the complicated relationship between aluminum and pH. Although aluminum is most toxic to fish at low pH, at very low pH aluminum can actually increase survival time. Also, the form of aluminum is very important since dissolved aluminum is most toxic and organically-bound aluminum is only slightly toxic. Aluminum levels at NED projects appear to be somewhat high and generally above the 0.1 ug/l level at which toxicity problems are found (in waters with certain characteristics such as low levels of pH and calcium); however, only total aluminum measurements were made. Additional measurements to determine the form of aluminum will be needed to determine the threat to sensitive aquatic life at NED projects.

Projects were ranked as to their present acidification and susceptibility to further acidification by aluminum concentration, alkalinity concentration, calcite saturation index, and Van Slyke's buffer values. The results show North Hartland Lake is the best protected from and Tully Lake is the most susceptible to the effects of further acidification. The other projects are in between with no definite order amongst them.

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1. AUTHORITY

This report is prepared in accordance with ER 1130-2-415, "Water Quality Data Collection, Interpretation, and Application Activities", dated 28 October 1976; and ER 1130-2-334, "Reporting of Water Quality Management Activities at Corps Civil Works Projects' dated 30 April 1986. These regulations establish guidelines for conducting and reporting water quality control management responsibilities at Corps Civil Works facilities.

2. INTRODUCTION

"Acid rain" is the name given to the phenomenon where sulfur and nitrogen emissions are transformed in the atmosphere into acidic compounds, transported often long distances and then precipitated in wet or dry forms. It is generally accepted that acid rain has increased the acidity of natural lakes and ponds in areas of New England where the soils in the watershed are of granitic origin and poorly buffered. It is less certain what effects acid rain has on forest, agricultural land, and human health. The greatest debate is over what steps should be taken to control acid rain.

This study's goal does not try to resolve those questions or even summarize the collected scientific evidence. The latter has been done in many excellent articles including Acid Deposition, Atmospheric Processes in Eastern North America by the National Research council, 1983; and additional important data is continually reported in the scientific literature and the popular press. Rather, it is this study's intent to look at the water quality effects of acid rain on the streams and impoundments at NED projects.

Most of the research on acid rain involves measurements of acid deposition itself or the condition of natural lakes and ponds affected by acid rain. The effects of acid rain on streams and small man-made impoundments is a somewhat neglected area of research. This is because the condition of a lake or pond is easier to monitor, due to its long hydraulic detention time, than that of a stream or impoundment. In theory at least, the longer the hydraulic detention time, the slower a body of water will respond to change and, thus, the smaller the number of samples that will be required to monitor its condition. (Recent research has shown that this is not necessarily true. Keller (1988) found that even though the Metropolitan District Commission's (MDC)

Quabbin Reservoir, located in central Massachusetts, has a 3-year detention time, yearly changes in alkalinity within the reservoir and its main tributaries have occurred nearly in unison since 1960.)

Although the primary purpose of NED flood control projects is, as their name states, flood control, the streams and impoundments at NED projects are also managed for recreation and fish and wildlife. For these reasons, NED is concerned that acid rain may be affecting the suitability of some projects for recreation or aquatic habitat. It is the intent of this study to determine the extent to which acid rain is affecting water quality at NED projects, and to determine if there are any trends in the pH or acidity which are leading toward more serious effects. Future studies may deal with the effects of acid rain on the aquatic and terrestrial ecology of NED projects and how to mitigate any observed effects of acid rain on NED projects.

3. BACKGROUND

The acidity of water is determined by the concentration of hydrogen ions which is expressed in pH. The pH of a solution is the negative log of the hydrogen ion concentration. Water's ionization constant limits the pH of water solutions to a scale from 0 for strong acid solutions to 14 for strong base solutions. For comparison, the pH of lemon juice is 2.0, of carbonated soft drinks is 3.0, of tomatos is 4.2, of milk is 6.5, of human blood is 7.4, and of soap is 8 to 9 (Katzenstein, 1981).

A neutral solution has a pH of 7.0, and this would be the expected pH of clean rainwater. However, the atmosphere's 0.03 percent carbon dioxide dissolves in rainwater to form carbonic acid with a pH of 5.65 at 20°C (Bertinuson, et al, 1983). This is the generally accepted pH of "clean" rainwater, but rainwater even when it is not affected by anthropogenic emissions is not clean. Volcanos and geysers put sulfur oxides including sulfuric acid into the air and lightning and forest fires introduce nitrogen oxides including nitric acid into the air. In addition, natural sources put acid-neutralizing substances into the atmosphere such as ammonia from the decay of protein materials and calcium and magnesium compounds from dust and ocean spray.

What becomes apparent is that it is not the pH of clean rainwater that is needed as a reference, since rainwater is not clean, but the pH of rainwater unaffected by anthropogenic activities. Estimates of what this should be vary. Precipitation, from before the industrial revolution, preserved in glaciers and continental ice sheets show pH levels generally above 5.0 (Likens, et al, 1979) but below 5.6 (Katzenstein, 1981). Studies by Swiss works found pH levels of 6.0 to 7.6 in snow that fell in Greenland 180 years

ago (Likens, et al, 1979). More recent work by U.S. Army Cold Regions Research and Engineering Laboratory (CRREL, 1984) researchers measured the pH of uncontaminated firm (consolidated snow) from the South Pole at depths of 22 to 620 feet below the surface. Snow at these depths fell 40 to 2,000 years ago. Their measurements showed that a pH of 5.4 would be representative of natural background conditions.

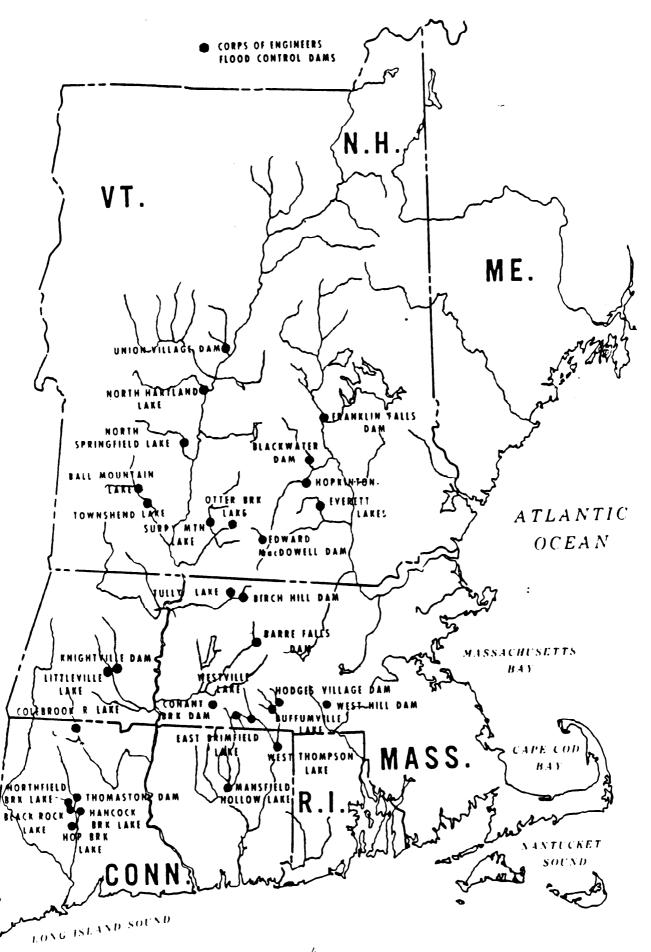
The pH of precipitation in parts of the world today that are far removed from major industrial centers is usually below 5.6, frequently below 5.0, and occasionally below 4.0. Low pH readings of 4.3 have been recorded in the South Pacific island of Pago Pago, 3.8 in Hawaii, 3.6 in the headlands of the Amazon River, and 3.4 in the remote northern territory of Australia (Katzenstein, 1981). While these levels may show that naturally contaminated rain may often have a pH below 5.0, it may also show that anthropogenic sources of sulfur and nitrogen are affecting the pH of rainfall worldwide.

In sum, the pH of "natural rain" varies, is somewhere below 5.6, and a good mean to use as a reference would probably be around 5.4.

The pH of streamflow unaffected by acid rain is even more difficult to determine than the pH of rainfall unaffected by anthropogenic emissions because of the number of other factors which can affect pH. One of these is the neutralizing effect of the soil. This neutralizing action has two parts; an uptake of nitrogen and sulfur compounds by plants in soils where those nutrients are deficient, and the buffering of acids by carbonates and bicarbonates in the soil. Another factor is swamps or bogs which can lower pH due to the release of organic acids from the decay of plant material. Buffering of pH occurs in lakes and reservoirs through the mixing of different pH inflows. Algae blooms and aquatic macrophytes can cause large daily fluctuations in pH: daytime photosynthesis uses up carbon-dioxide lowering the carbonic acid levels and converting bicarbonates to hydroxides and thus raising the pH as high as 10 or even higher; nighttime respiration adds carbon dioxide causing the pH to drop as low as 4 or even lower. Finally, pH levels can be affected by point and nonpoint source discharges and unusual watershed conditions such as acid mine runoff. All these factors must be considered in determining if the pH of the water is affected by acid rain.

4. NED'S WATER QUALITY MONITORING PROGRAM

NED's acid rain studies are an outgrowth of NED's water quality monitoring program. This program began in 1970 and includes 31 flood control projects. Figure 1 shows the locations of these projects.



The primary purposes of this water quality program are to protect public health at bathing beaches and recreation areas, understand the effects of project operations on water quality, aid in fish and wildlife management at Corps projects, and monitor trends which could affect water quality at these projects. In order to carry out this program, water quality data were collected in two ways. The first was through grab samples which were collected at all projects and analyzed for a variety of parameters including temperature, pH, dissolved oxygen, conductivity, nutrients, and heavy metals. The second type of data collection was through the use of automatic water quality monitors (AWQM) which were located only at selected projects and measured only temperature, pH, DO, turbidity, and conductivity.

Grab sample data collected at the 31 NED projects contains a large number of pH observations. These data were collected over a long period of time at a number of locations at each project. A great deal of baseline information is contained in these data; however, it also has its limitations. It was collected essentially on a random basis with respect to rainfall and runoff conditions, the number of samples and time of year that samples were taken varied from year to year and project to project, and many stations were changed or deleted during the program so that a full record does not exist for all stations. The grab sample data are best used for trying to identify long term trends in pH.

Data from the AWQM's is better for identifying the effects of specific events, although it can also be used to identify trends. AWQM data is recorded every 4 hours continuously and can accurately describe diurnal variations in pH and transient changes in pH due to runoff from acidic rainfall events.

Data from the AWQM's also has its limitations. Monitors were located only at project discharge stations; consequently, in those projects with permanent pools the recorded pH includes the effects of mixing with the water in the pool. Monitors were not located at all projects. The AWQM record is no more than a few years long at any project, and, finally, the monitor record is interrupted by mechanical failures of the pH probe, the pump, or the monitor itself.

Some heavy metals and alkalinity analyses were made on grab samples collected as part of the NED water quality management program. However, these data were not collected with the intention that they be used to document either long term changes due to acid precipitation or short term changes due to specific acid runoff events. They do supply a baseline to compare observed conditions against expected conditions, but the usable data record is too short and too sparse to identify trends in these parameters.

5. NED'S ACID RUNOFF STUDY

- a. General. With the water quality sampling equipment already on hand and a large data base in the files, only a few changes were needed to initiate NED's acid runoff study from the existing water quality management program. The collection of parameters such as alkalinity and aluminum, which are affected by acid rain, was increased, and, where possible, AWQM's were moved to those projects best suited to the study of acid runoff. Because of the other data needs of NED's water quality program, monitors were not sited only for the acid rain study.
- 1984 Interim Report. In November 1984, NED issued and interim report entitled "Effects of Acid Precipitation on NED Projects." This report summarized NED's beginning study of the effects of acid precipitation on river pH levels at 7 of its reservoir projects. No measurements of acid rain itself were made as part of this study, and no assessment of the effect of acid rain on the ecology of the projects was performed. This study used runoff water quality data collected by NED with automatic monitors in 1982 and 1983 and by grab samples since 1970, and acid rain data collected by others. Results showed that average pH levels at the projects studied have remained essentially constant since NED began collecting data. The principal effect of acid rain at NED projects appeared to be sudden short drops in pH during particularly acidic storms. However, correlating drops in river pH with heavy acid loads in rainfall was very difficult. This was attributed to a lack of site-specific rainfall data, and the complexity of the relationships between rainfall and runoff water quality.

Mean river pH between and during most storms at all projects was within or close to the 6.5 to 8.0 level which is desirable for most water uses. This appeared to be due to natural alkalinities which tend to buffer acid rain effects. However, Tully and Otter Brook Lakes had alkalinities so low that any significant increase in acid rain could completely deplete the water's buffering capability. Acid rain was also thought to be possibly increasing aluminum levels at the projects.

A ranking of the 7 projects according to their degree of acidification, and susceptibility to further water quality degradation should acid rain increase, was made based on alkalinity, aluminum, and calcium levels, and mean pH. The resulting ranking was, in order of decreasing susceptibility,

Tully Lake
Otter Brook Lake
Hodges Village Dam
Littleville Lake
West Thompson Lake

Thomaston Dam Union Village Dam.

Tully Lake was clearly at the top of the list having the lowest mean pH (5.84–S.U.) and barely any remaining alkalinity (mean = 1.7 mg/l as $CaCO_3$). Otter Brook was a definite second with a low mean pH (6.31), and a very low alkalinity (mean = 2.9 mg/l as $CaCO_3$). Union Village Dam was unquestionably at the bottom of the list with an alkaline mean pH (7.34), plenty of alkalinity to buffer additional acid loads (76.2 mg/l as $CaCO_3$), and the lowest aluminum concentrations. Thomaston was the next least acidified as indicated by its neutral pH (7.06) and relatively high alkalinity (21.4 mg/l as $CaCO_3$). The order of the other three projects, other than being between Otter Brook and Thomaston, was less clear.

An attempt was made to apply a simple method developed by Henriksen (1970) for determining the degree of watershed acidification; however, this method could not be adapted to NED projects.

c. Continuing Studies. In continuing studies since the 1984 report, the number of projects included was increased to ten. Union Village Dam was dropped because its highly buffered waters were the least susceptible to and the least likely to show any response to the effects of acid rain. Birch Hill and Barre Falls Dams in Massachusetts and North Hartland Lake in Vermont were added. These ten projects were selected to give a good north to south distribution, to include all four states with NED projects, and to include dry-bed reservoir projects and projects with pools. The northernmost project selected was North Hartland Lake in Vermont. The other projects in this study, from north to south, are Franklin Falls Dam and Otter Brook Lake in New Hampshire; Birch Hill Dam, Tully Lake, Barre Falls Dam, Littleville Lake, and Hodges Village Dam in Massachusetts; and West Thompson Lake and Thomaston Dam in Connecticut. Figures 2 through 11 show the individual projects and the locations of the AWQM s and grab-sampling stations. gives a summary of each project's hydrologic and hydraulic characteristics.

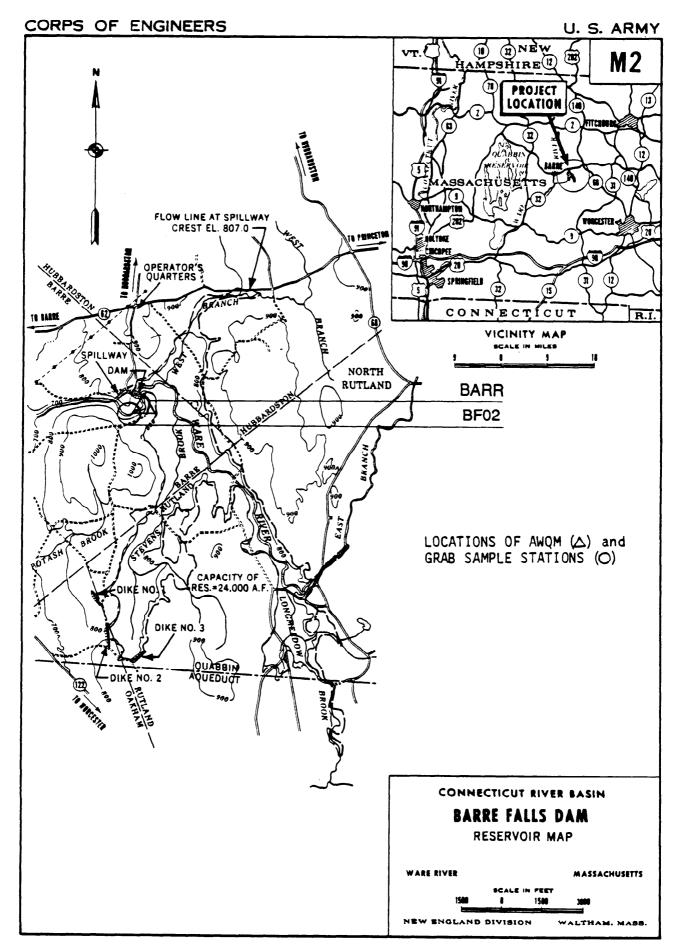
The AWQM's used in these studies were Schneider Instrument Robot Monitors model RM25AT. They were set to measure pH in the range of 2 to 12 Standard Units (SU) with an accuracy of plus or minus 1 percent.

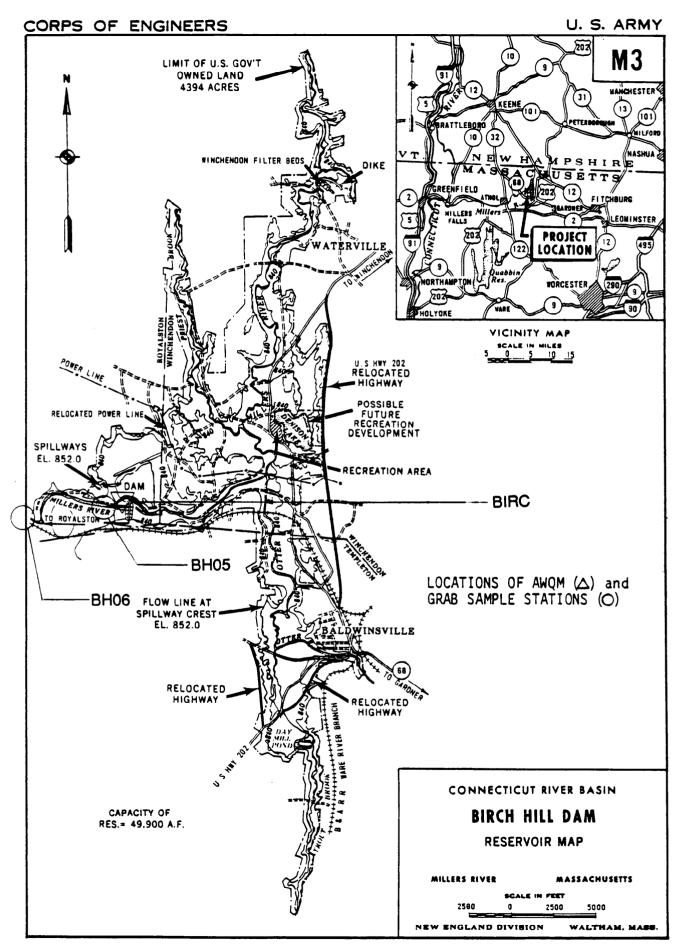
Monitors were installed near the discharge channel below the dam as shown in figures 2 through 11. Water from the discharge was pumped up into the monitor for analysis. These monitors are generally installed in the spring and removed in late fall on a yearly basis.

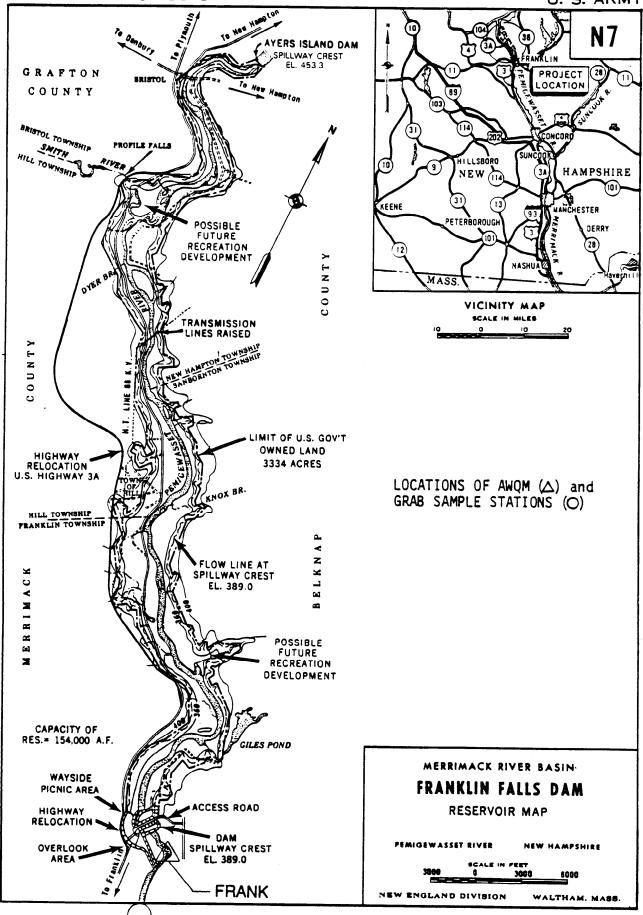
TABLE 1
PROJECT CHARACTERISTICS

		Duringer		Permanent	Pool	Average	Annual Runoff
Project	Location	Drainage Area (sq. mi.)	Volume (ac-ft)	Surface Area (acre)	Control	Flow (cfs)	Flow/Sq. Mi. (CSM)
Barre Falls	Ware River	55	Dry-bed	Reservoir		94	1.7
Birch Hill	Millers River	175	Dry-bed	Reservoir		305	1.7
Franklin Falls	Pemigewasset R.	1,000	Dry-bed	Reservoir		2,190	2.2
Hodges Village	French River	31.1	Dry-bed	Reservoir		55	1.8
Littleville	Middle Branch Westfield River	52.3	9,400	275	Weir	104	2.0
Otter Brook	Otter Brook	47	720	70	Weir	78.7	1.7
Thomaston	Naugatuck R.	97.2	Dry-bed	Reservoir		197	2.0
Tully	East Branch Tully River	50.4	1,500	305	Low level gate	e 81	1.6
West Thompson	Quinebaug R.	172	1,200	200	Weir	311	1.8

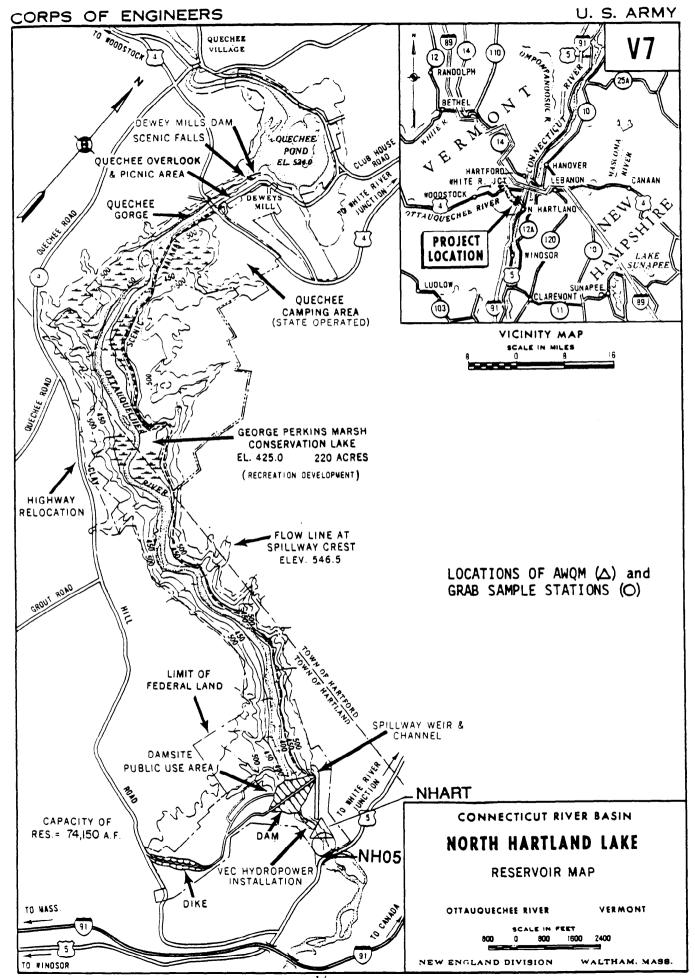
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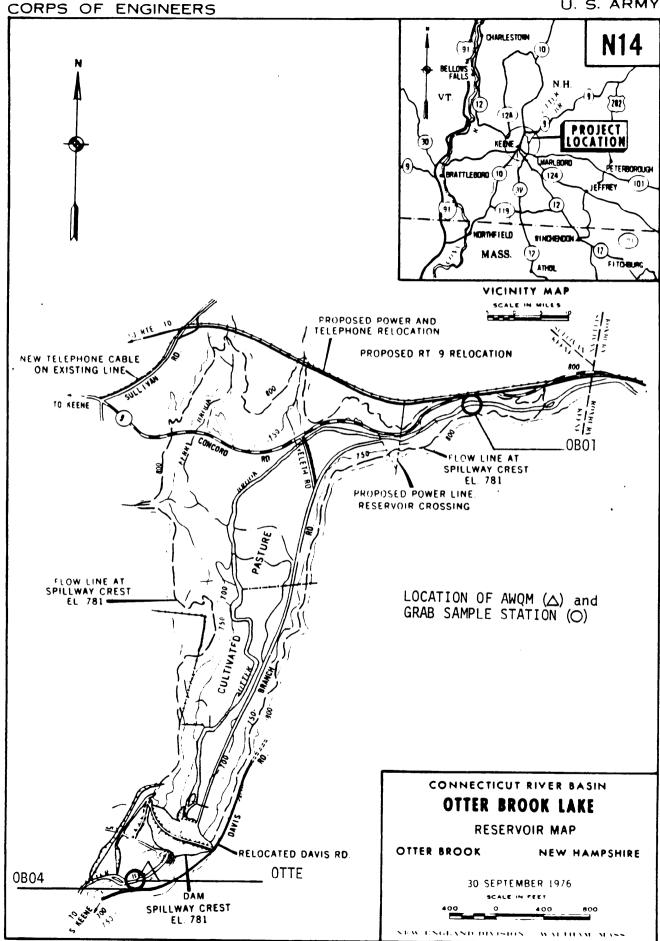


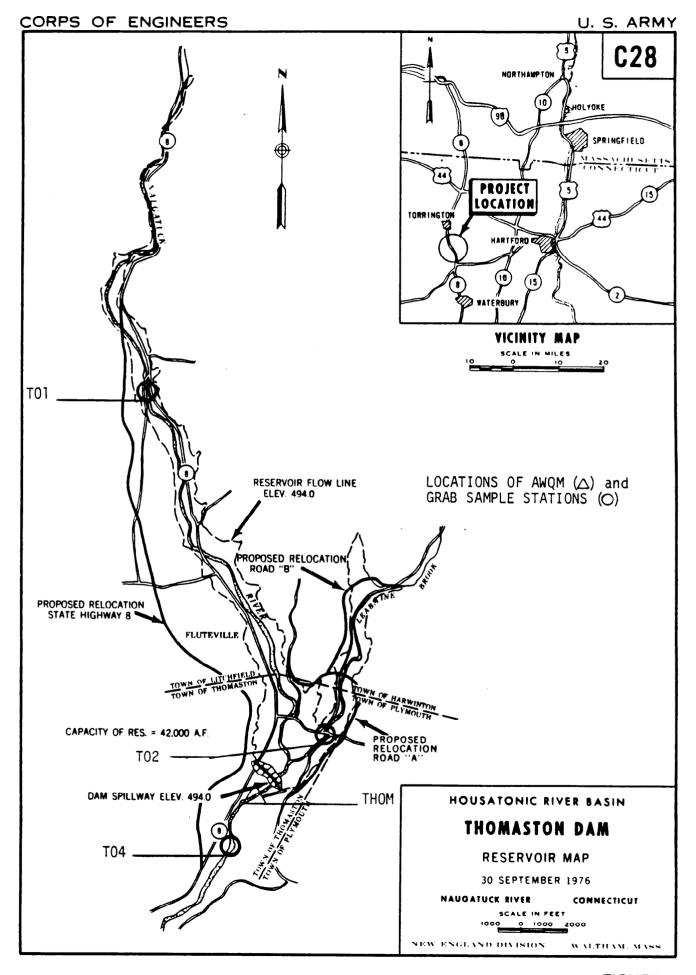


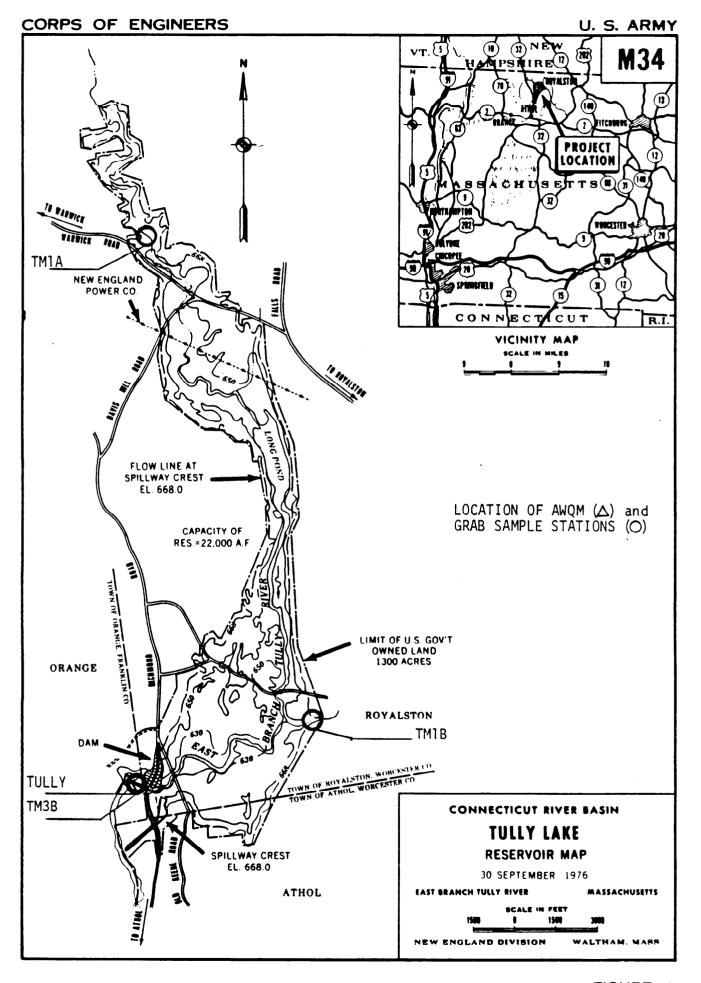


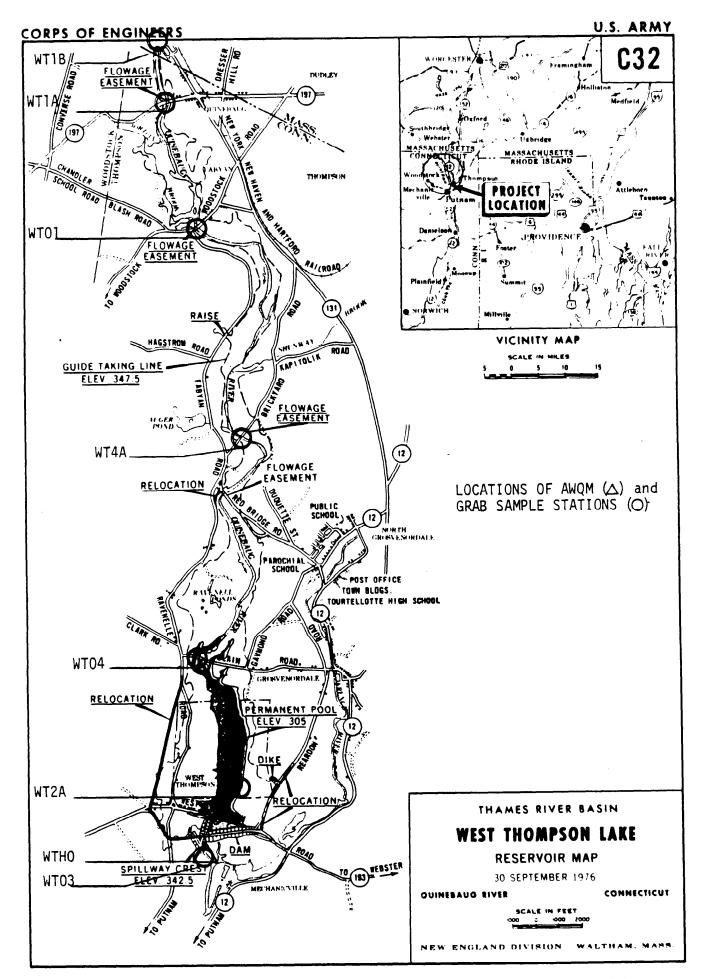
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Appendix A contains annual plots of the complete AWQM pH records from these stations for the years 1982 through 1987.

6. PRECIPITATION DATA

a. Precipitation Data Collection Methods. NED began collecting precipitation data at four projects in 1987: Buffumville Lake, Thomaston Dam, North Hartland Lake, and Barre Falls Dam. These projects were chosen based on factors including a North-South geographic spread and the ability of the project managers to participate in the study.

Precipitation data collected by NED was supplemented by data collected by other organizations and individuals. These included the National Acid Deposition Program (NADP), the U.S. Geological Survey (USGS), the Water Resources Research Center at the University of Massachusetts at Amherst, and Holy Cross College in Worcester, Massachusetts. Figure 12 shows the locations of the precipitation data collection stations, and table 2 gives descriptions of these stations.

Precipitation data were collected in different ways. The National Acid Deposition Program data (Scott 1988) and USGS data (Kulp 1987) were collected using wet-sensing precipitation collectors which opened to collect only wet deposition. NADP samples were analyzed once a week, while USGS data were collected and analyzed on an event basis. University of Massachusetts data (Walk 1987), Holy Cross College data (Vidulich 1987), and NED data (Condike 1987) were collected on an event basis using an open polyethylene container; as there was no way to keep out dry deposition, that was also included in the samples.

Appendix B contains the precipitation data collected by NED.

- b. Application of Precipitation Data. In order to evaluate the acid load of various storms, the amount and pH of storm events were combined to compute the pounds of acid which fell on each square mile of watershed. This was done by assuming that two-thirds of the acidity in rainfall comes from sulfuric and one-third comes from nitric acid. Although this method ignores the effects of atmospheric carbondioxide, which alone will reduce the pH of rainfall to 5.65, for the purposes of comparing storms it is quite adequate. By discounting the effects of atmospheric carbon-dioxide, this method is least accurate at pH above 5.6, but most accurate at the lower pH's at which most storms occur.
- c. Kriging. Data from different precipitation collection stations was combined using a modified interpolation technique called Kriging (Finkelstein 1984). It was developed by D. G. Krige a gold-miner in South Africa.

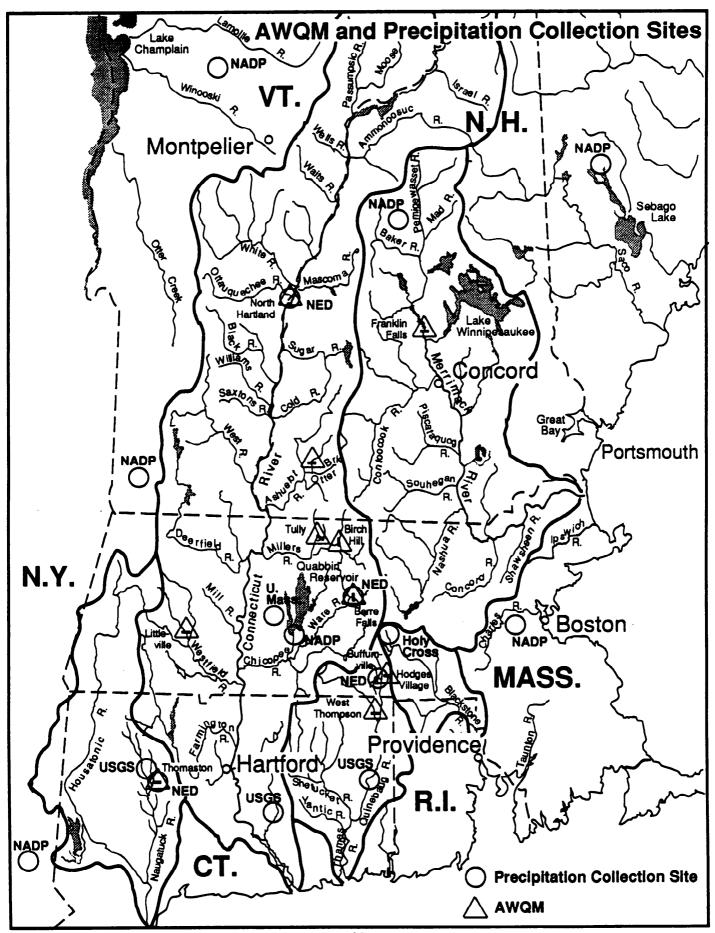


TABLE 2

PRECIPITATION DATA COLLECTION STATIONS

Collecting	Station	Station
Agency	<u>Name</u>	Location
NADP NADP NADP NADP NADP NADP	Bridgton Hubbard Brook Underhill Bennington East Quabbin West Point	Western Maine Northern New Hampshire Northern Vermont Southern Vermont Eastern Massachusetts Central Massachusetts Southeastern New York
Holy Cross	Holy Cross	Central Massachusetts Central Massachusetts
USGS	Wauregan	Eastern Connecticut
USGS	North Westchester	Central Connecticut
USGS	Thomaston	Western Connecticut
NED	North Hartland	Central Vermont
NED	Barre Falls	Central Massachusetts
NED	Buffumville	South Central Massachusetts
NED	Thomaston	Western Connecticut

In brief, Kriging assumes that the covariance between two points depends only on the distance between them.

The acid loading at each project was computed on a weekly basis by multiplying the distance from the center of the watershed to each precipitation collection station times the acid loading at that station, summing these products for all stations, and then dividing this sum by the sum of the distances. Table 3 gives an example of this sort of Kriging.

Table 3 Kriging

Precipitation Collector	Acid Load	Distance from Collector to	Distance Times
	lbs/sq mi	Project X	Acid Load
A	12	24	288
В	18	36	648
C	7	50	350
	Sum	110	1.286

Acid loading at Project X = 1,286/110 = 12 lbs/sq mi.

Because about half the precipitation data were collected on an event basis and the rest were collected on a weekly basis, all data were combined to give weekly acid loadings. Where data collected on an event basis included dates which overlapped two weeks, the data were included for the week in which most of the storm occurred. For example: if a storm lasted from 6-8 September, it would be counted as occurring in the week of 7-13 September. When a storm evenly overlapped two weeks, it was counted as occurring in the first week. It should be noted that most storm events were collected in one day and it was quite rare for a storm event to overlap collection weeks.

d. Annual Acid Loading Plots. The time and effort required to compute acid loadings were too great to allow these computations to be performed for all ten projects involved in the continuing acid rain study. Therefore, the number of projects was limited to three: Franklin Falls Dam in New Hampshire, Tully Lake in Massachusetts, and Thomaston Dam in Connecticut. These projects were selected to give a good North-South distribution.

Weekly acid loadings for Franklin Falls Dam, Thomaston Dam, and Tully Lake were plotted and are presented in figures 13 through 27. Because of the amount of work involved in calculating and preparing these plots, only those years between 1982 and 1987 were included for which automatic water quality monitor data were available. These plots show that while acid-loading occurs year-round, the peak acid events

tend to occur during the summer. A possible explanations for this phenomenon is that during the warmer summer months the chemical transformations which convert sulfur and nitrogen emissions into acids occur more quickly and completely. Other possible explanations include different wind patterns in the summer and winter, or different emission rates.

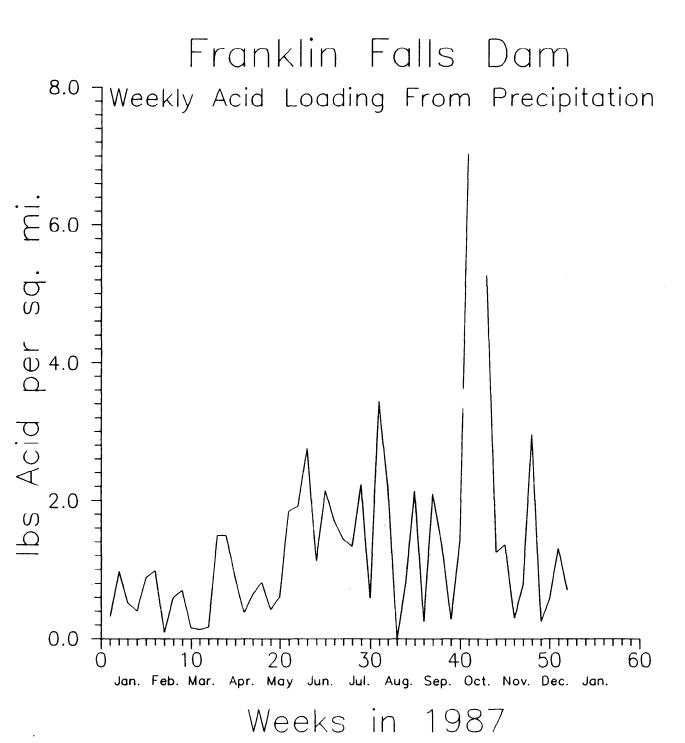
Weekly acid loadings for Franklin Falls Dam, Thomaston Dam, and Tully Lake were plotted against pH plots from the AWQMs in 1987 and are presented in figures 28 through 30. The results of these plots are discussed in the following two sections. There was not enough time to prepare these plots for the years from 1982 through 1986.

e. <u>Discussion</u>. The expected effect of an acid load in rain falling on a watershed would be a decrease in the pH of the runoff. How much of a drop will occur, however, depends on the ability of the watershed to neutralize the acid load. In order to determine what sorts of relationships to look for between acid loading and acid runoff, a literature search was conducted on the responses of small watersheds to acid loads.

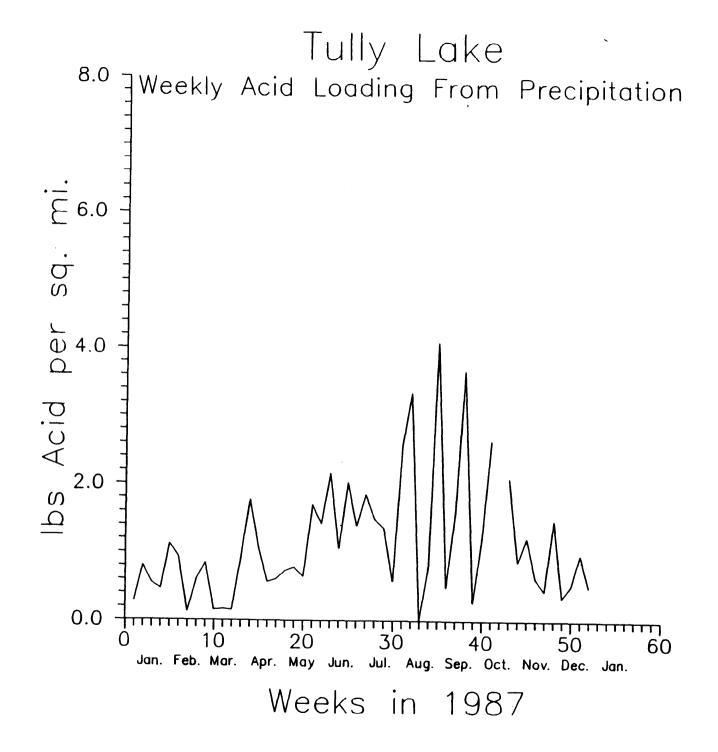
An acid load falling on a watershed will be neutralized in a variety of ways to varying degrees by different methods depending on the characteristics of the watershed. These include soil depth, vegetation, runoff characteristics, fires, beavers, and anthropogenic activities. The result is that even small watersheds close together can respond quite differently to the same acid loading. Consequently, attempts to broadly classify areas with regard to susceptibility to acidification based on general geologic features are not always successful.

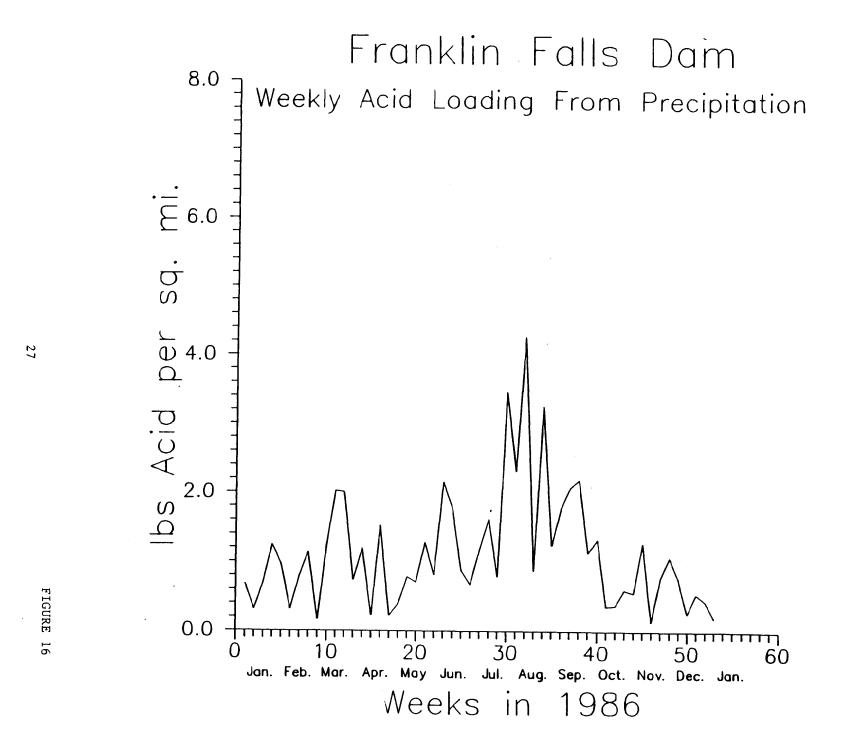
Haines and Akielaszek (1983) conducted a survey of 226 headwater lakes and low order streams in the six New England states. The waters selected had relatively little direct human disturbance, and were low in color thus eliminating those bodies of water which might be significantly acidified by organic acids. Of the physical factors measured, the ones most highly related to buffering capacity and acidity were bedrock geology and, to a lesser extent, soil cation exchange capacity. A sensitive lake or stream, as determined by alkalinity, was nine times more likely to be found in an area where bedrock was low in buffering capacity. A sensitive lake or stream was three times more likely to be found in an area where soils were low in cation exchange capacity. Soil class was correlated with bedrock class, with sensitive soil classes largely found in areas where bedrock was also sensitive. In headwater areas soils tend to be thin and therefore may be less important than bedrock in determining water chemistry.

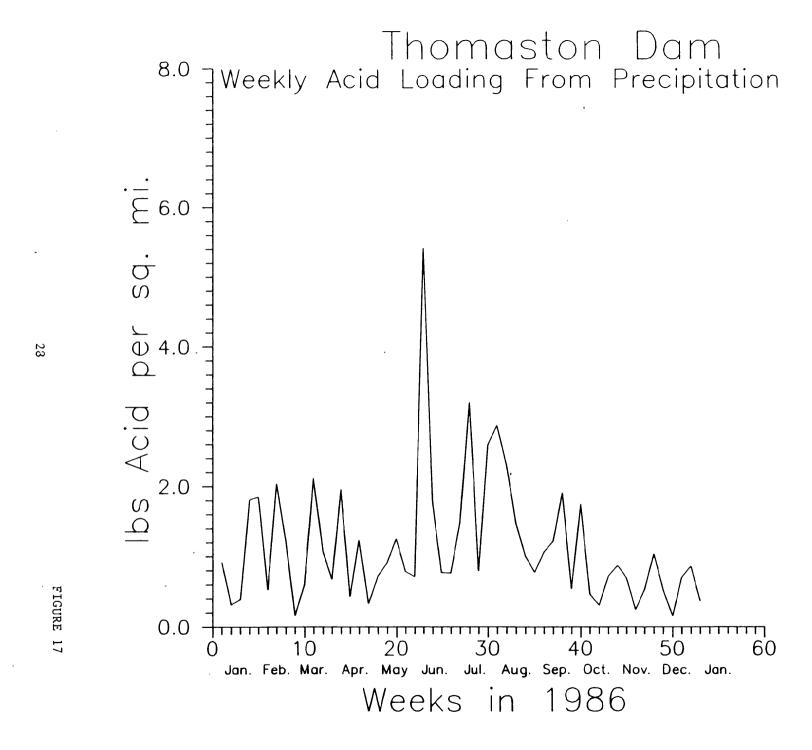
The only other physical factors of importance were lake area and stream order. Lakes of all sizes were low in

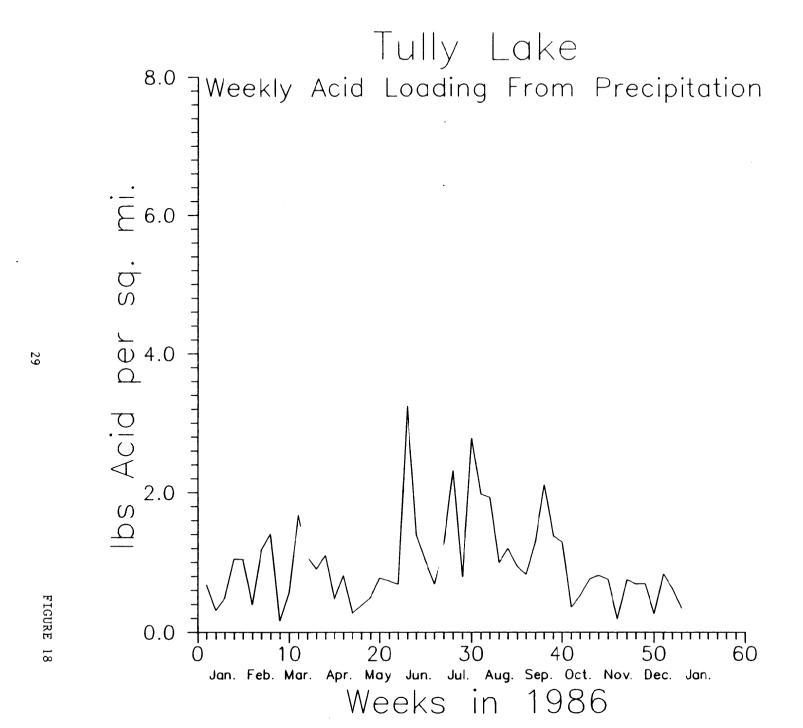


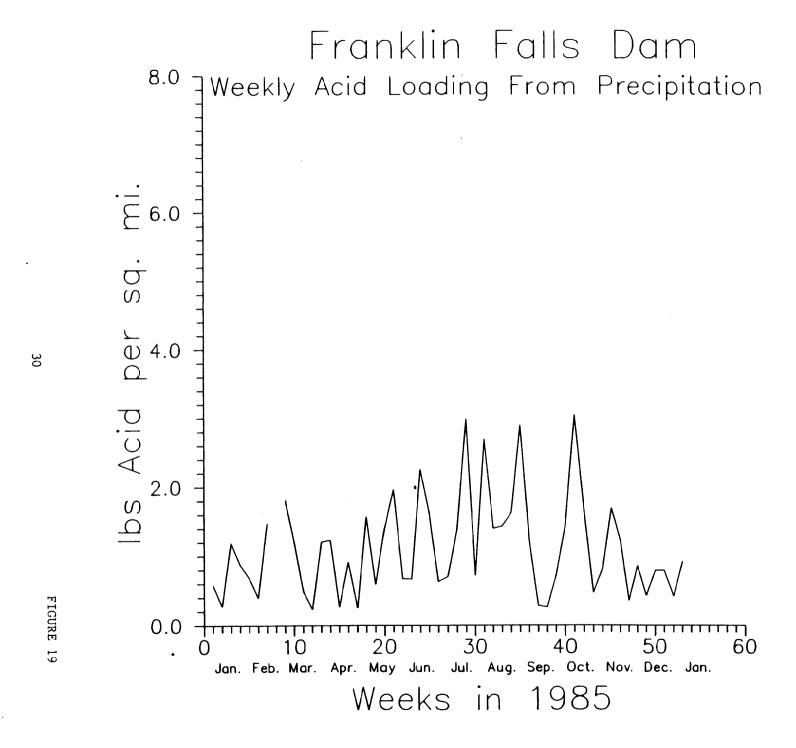
FIGURE

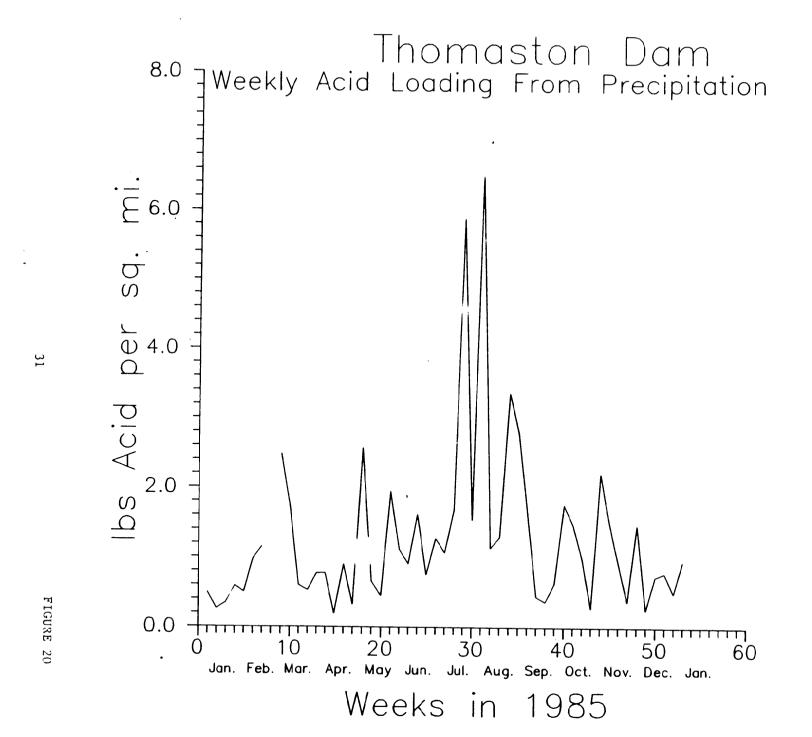


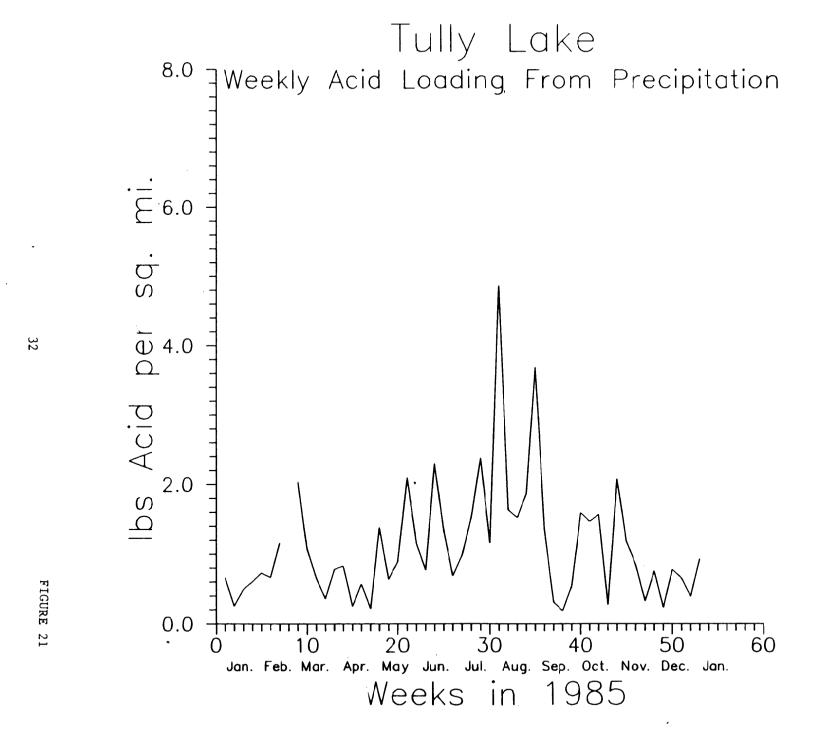


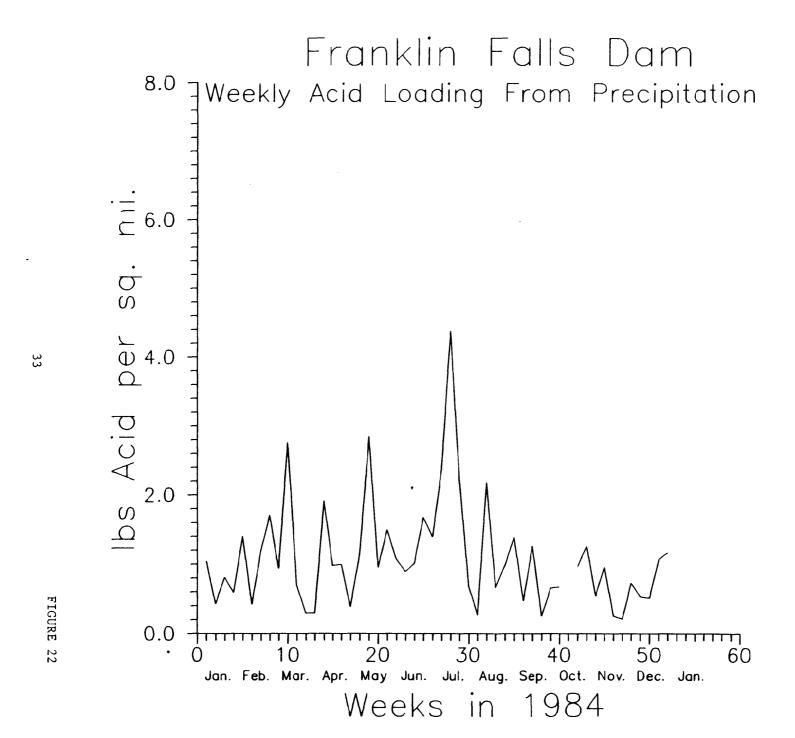


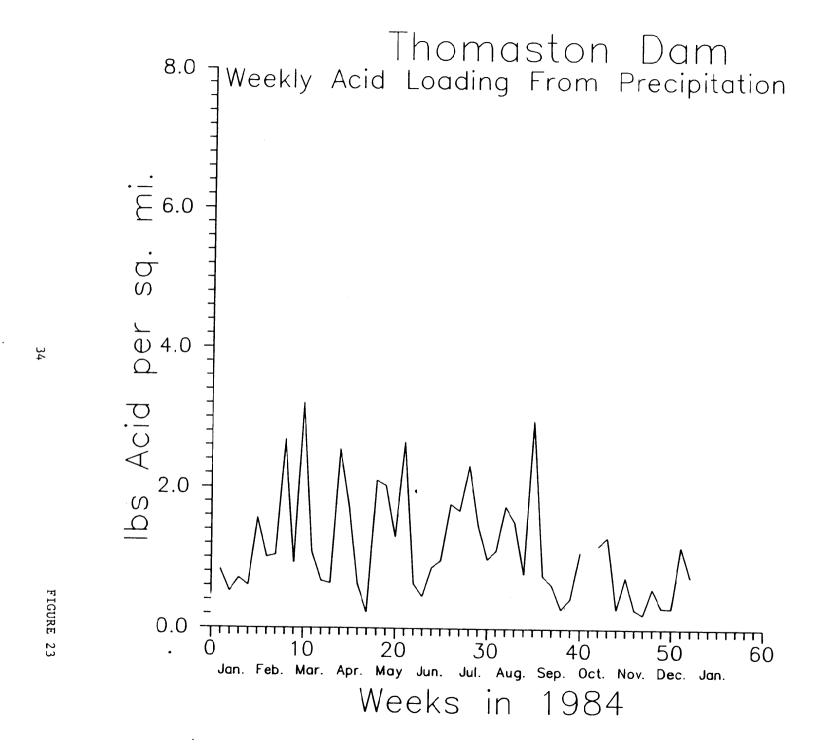


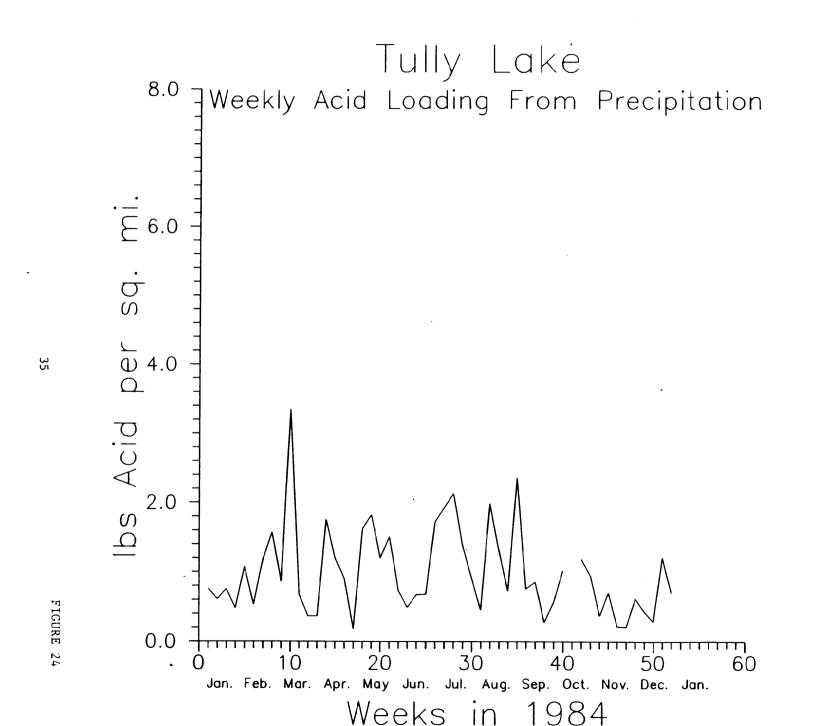


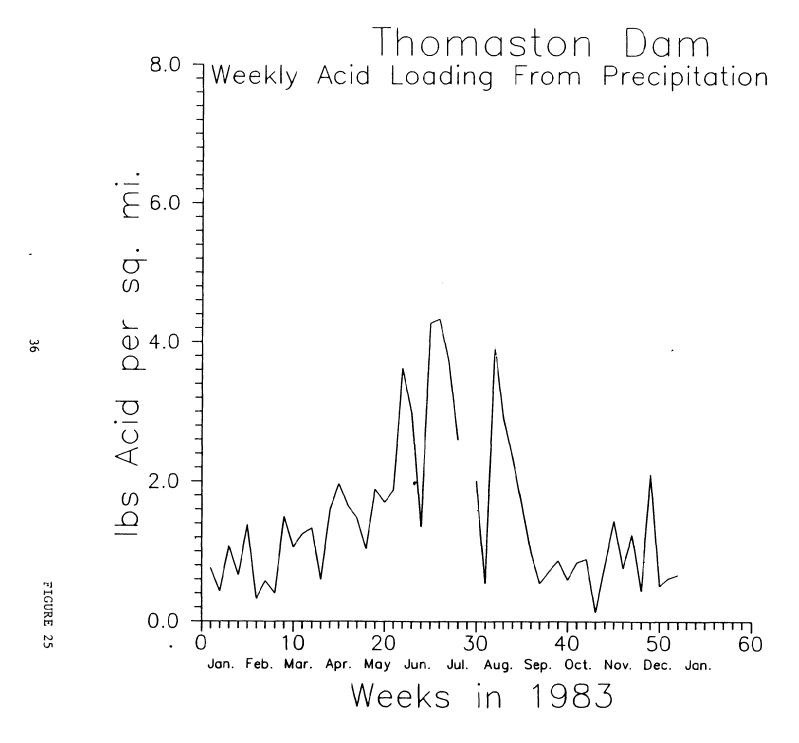


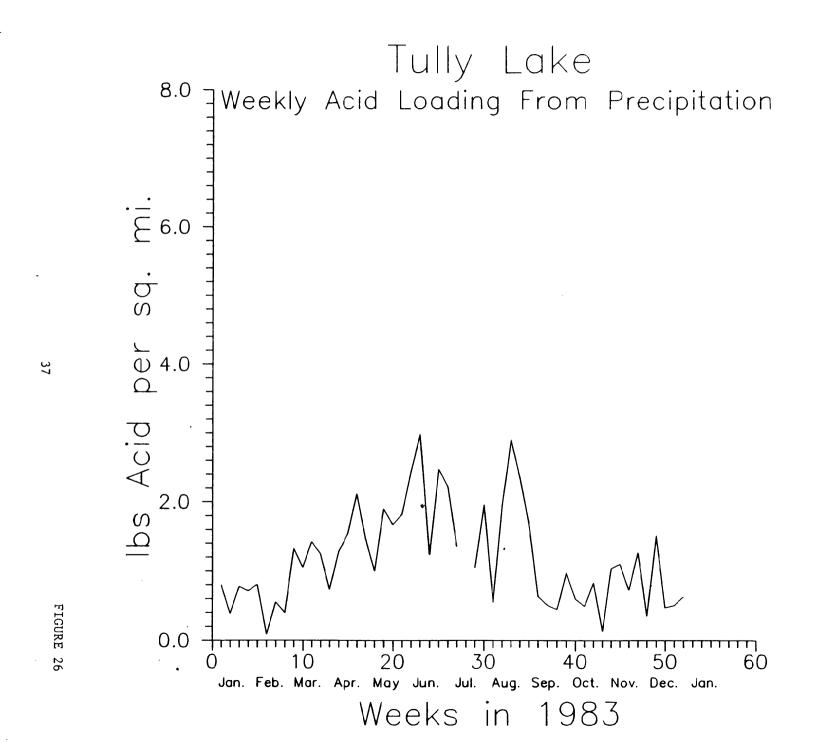


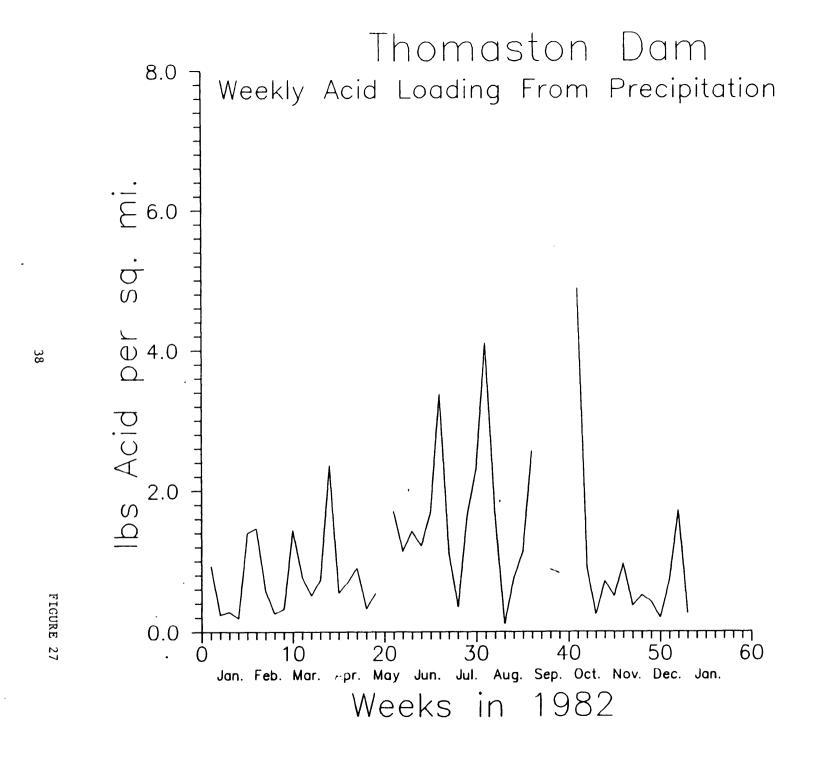




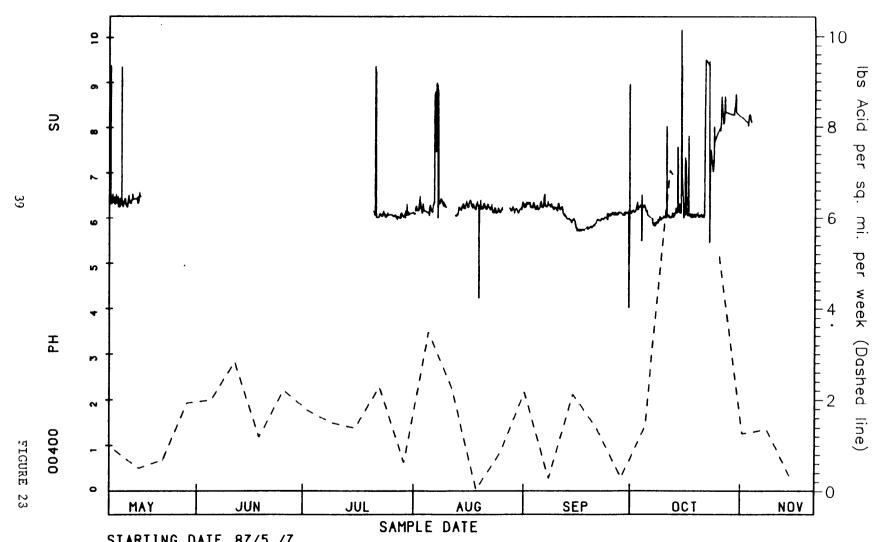








STORET
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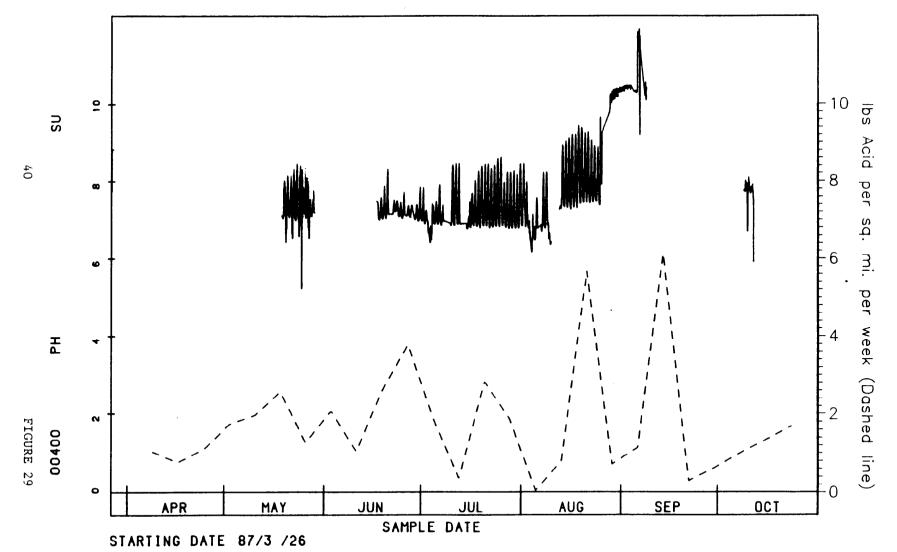


STORET EXP291A THOM EXPW0M291A 41 41 11.0 073 03 55.6 1 THOMASTON DAM IMPOUNDMENT, THOMASTON, CT. LITCHFIELD 09005 CONNECTICUT 010200 NORTHEAST HOUSATOLIC RIVER

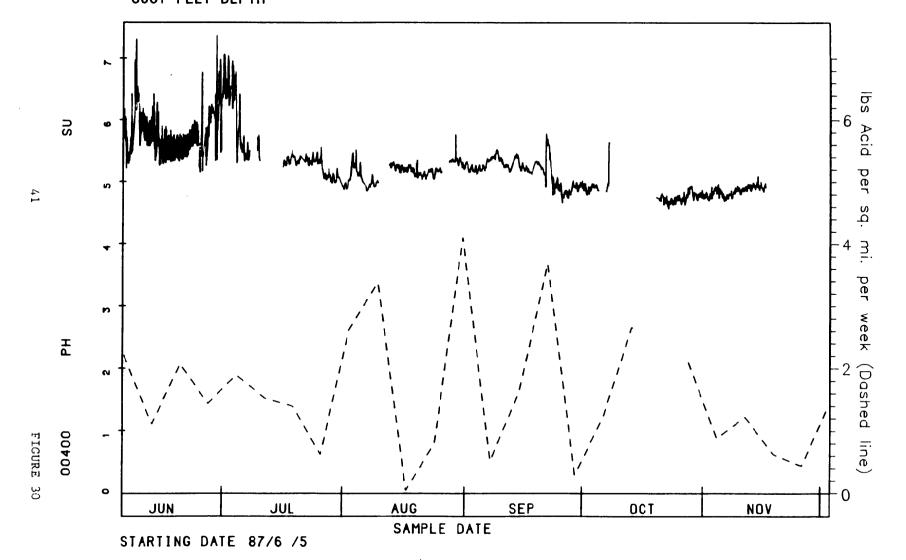
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25027 MASSACHUSETTS WORCESTER
NORTHEAST 010400
CONNECTICUT RIVER
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alkalinity but only lakes of 20 hectares area or smaller were acidic. Higher order streams were higher in pH and alkalinity. This suggests that some factor related to watershed size may be an important factor in neutralizing acid deposition: watershed size was correlated with lake pH for lakes in Maine.

Haines and Akielaszek concluded that a substantial portion of the headwater lakes and low order streams in New England are vulnerable to acidification, and that alkalinity is the best measure of vulnerability. Bedrock geology was the best physical factor that could be used to predict surface water alkalinity, and thus vulnerability to acidification, but a substantial portion of the waters that were predicted to be vulnerable were not.

In a study of sub-basins of Caldwell Creek in central Massachusetts, Leonard et al. (1984) found that groundwater velocity and hydraulic gradient have the most statistically significant influence upon groundwater chemistry of the various hydrologic characteristics of the individual areas. Groundwater with rapid velocity and steep hydraulic gradient had lower pH and low specific conductivity, whereas groundwater with slower velocity and low hydraulic gradient had neutral pH and higher specific conductivity.

Another study of Caldwell Creek watershed was performed by Batchelder et al. (1983). They found that sub-watersheds with large percentages of exposed or near-surface bedrock or stratified drift deposits are less effective in buffering the incoming acidity than are areas covered by relatively thick deposits of till, indicating that surficial materials play a significant role in the ability of a watershed to neutralize acidic precipitation. Stream water pH in a till watershed averaged 6.07, whereas the pH of a predominantly stratified drift-bedrock watershed was much lower at 5.35 SU.

Yuretich et al. (1986) in a study of small watersheds in central Massachusetts found that in all watersheds, hydrogeology was the most important control on water composition: the longer the contact time of water in the aquifer, the greater the specific conductivity regardless of the type of surficial material forming the aquifer. the average residence time of groundwater in all these watersheds was on the order of one year, this was sufficient time to effectively neutralize all mineral acidity in the groundwater, regardless of the aquifer mineralogy. A simple rule applied: the greater the amount of baseflow in a stream, the more effective will be the overall acid neutralization in that stream. In central Massachusetts, greater baseflow results from more extensive areas of stratified drift; therefore, it should be possible to estimate effectively the acid-neutralization potential of a particular watershed by a simple mapping of the stratified drift deposits. Their

studies showed that weathering of plagioclase feldspar was the dominant process in acid neutralization.

In studies of the MDC's Quabbin Reservoir tributaries, Rittmaster et al (1988) estimated that weathering and ion exchange neutralize 90 percent of the acid load to the Swift River basin and 81 percent of the acid load to the Fever Brook basin. The remainder of the acid in the watershed is neutralized through other mechanisms such as nitrate uptake by vegetation and alkalinity production by aquatic plants and micro-organisms. That such large percentages of acid neutralization are due to soil interactions encourages broad generalizations about the susceptibility of waters to acidification based on such factors as general geologic features. For large watersheds, this is probably true and agrees with the findings of Haines and Akielaszek (1983) that watershed size could be correlated with lake pH.

The most ambitious attempt to make regional estimates of the chemical status of lakes within a specific region or subregion is being performed by the U.S. Environmental Protection Agency in its Eastern Lake Survey (ELS) (Linthurst 1986). Part of the National Surface Water Survey, which is a contribution to the National Acid Precipitation Assessment Program, the ELS had three primary objectives:

- 1. Determine the percentage and location of lakes that are acidic in potentially sensitive regions of the eastern U.S.
- Determine the percentage and location of lakes that have low acid neutralizing capacity in potentially sensitive regions of the eastern U.S.
- 3. Determine the chemical characteristics of lake populations in potentially sensitive regions of the eastern U.S. and provide the data base for selection of lakes for further study.

To accomplish these objectives, in the fall of 1984, single samples were taken from 1,612 lakes from the Northeast, Upper Midwest, and Southeast. Chemical variables and physical attributes thought to influence or be influenced by surface water acidification was measured for each lake. The results of these measurements form the ELS data base.

The states involved in the ELS were divided into three regions: the Northeast, Upper Midwest, and Southeast. Each region was divided into subregions. Each subregion was further stratified by alkalinity map class, which differentiated among areas within each subregion based on the surface water alkalinity range expected to dominate in different areas within these subregions.

The ELS tried to map regions where lakes would be expected to have similar chemical characteristics without

determining what watershed characteristics were affecting lake chemistry.

However, the variable response to acid deposition of even closely located watersheds was shown in the work of Buso et al. (1984). In studies of six similar, remote ponds in the White Mountains of New Hampshire that were all within 12 miles of each other and should have received the same acid loading Buso found that their water chemistries were quite different. For example, the volume-weighted pH of the ponds ranged from 4.5 to 6.0 SU. Differences in pond water chemistry was attributed to differences in watershed geology, disturbance, and hydrology. Deeper soils and more weatherable minerals in the watershed produced longer flow paths, higher pH and alkalinity, and lower sulfate levels in the inlet streams.

Effects of past watershed disturbance on pond pH was less clear, but certain tendencies were found. Deciduous forests tend to produce less acid runoff than coniferous forests as found also by Klein (1982) in studies of Vermont soils on Camels Hump Mountain; this probably has more to do with the acidity of decomposing pine litter than a different response to acid deposition. However, the change in shade cover from coniferous to deciduous forest also affects pond acidification. Under a deciduous tree cover, the snow tends to melt earlier and inlet streams are warmer. Earlier snowmelt decreases opportunities for mixing of acidic runoff with pond water since the pond is more strongly stratified in early spring. Similarly, warmer streamwater will mix less deeply into a pond in the ice-free season. These hydrologic changes may decrease the susceptibility of a pond to acidic deposition. Logging, fire, and agriculture tend to reduce nutrients in the watershed which causes more of the nitrate in nitric acid deposition and sulfate in sulfuric acid deposition to be taken up by plants and thus neutralized. However, these are short term effects which are eliminated by revegetation. Severe fires can result in shorter water pathways by removing vegetation, reducing soil depth, and exposing bedrock. Thus, they reduce the long-term acid buffering capacity of burned watersheds. This is of special significance in New Hampshire where poorly buffered areas are already substantial and deposition is acidic. Deeper, stratified ponds tend to have longer and deeper anaerobic periods in their hypolimnions. Reduction of sulfate during anoxia can produce significant acid neutralization.

At one of the ponds under study, Black Pond, beavers returned to the watershed during the study, and their immediate effect on water quality was measured. Beaver impoundments caused a drop in pH which was attributed to the release of organic acids from drowned vegetation and soils. Beaver activity also increased the size of the hypolimnion resulting in more sulfate reduction. Measurements of the

charge for organic anions in the pond water, as calculated by the methods of Oliver et al. (1983), ranged up to 92 percent of the sulfate charge. This showed that organic acid produced in part by beaver activities can be as important to Black Pond's total acidity as sulfate derived form acidic deposition. Beavers can also add dissolved organic carbon (DOC) which can be critical to maintaining a low Al:DOC ratio. Driscoll et al (1980 138) showed that at low pH (less than 5.5) aluminum is less toxic if large amounts of DOC are present.

At Cone Pond, another pond included in the study, Buso found sulfate reduction occurring in the anoxic bottom waters during the winter. This agrees with the suggestions by Kelly et al. (1982) that when enriched lakes receiving acid precipitation become anoxic, sulfate reduction is favored over other bacterial processes because there is abundant sulfate in such lakes. Sulfate reduction is accomplished by certain anaerobic bacteria and produces bicarbonate ion, whereas other more commonly found bacterial processes do not. However, the alkalinity produced by this sulfate reduction is only permanent if the sulfide produced is precipitated as ferric-sulfate which requires high iron concentrations.

Buso's (1984) observations of processes in Cone Pond lead to the suggestion that winter stratification under ice cover may provide a recovery period for ponds that receive acidic streamwater inputs, and that a surprising amount of alkalinity can be produced in anoxic waters. Cone Pond showed the importance sulfate reduction may have in oligotrophic freshwater ponds. Similar results were found in studies of Cape Cod ponds by Giblin et al. (1988). Their studies showed natural reduction of sulfate (primarily to iron pyrite) could produce 20 to 160 milli equivalents of alkalinity per year. Giblin also found that additional alkalinity could be produced by the reduction of nitrate. Alkalinity lost by uptake of ammonium was half that gained by nitrate reduction.

The mineralogy of geologic formations in New Hampshire is very complex. Some granites can neutralize acids, while some metasedimentary rocks are inert or even acidic. Buso found a granitic watershed much better buffered than a metasedimentary watershed. He concluded that the characterization of a watershed's buffering capacity or aquatic chemistry based on rock types may be misleading. He suggested it would be more appropriate to characterize a watershed by the minerals present than by general rock types.

Buso's studies pointed out that a regional approach to classifying the sensitivity of streams and lakes to acidification is often inappropriate for individual streams and ponds. Factors not easily obtainable from regional maps, such as stream hydrology, contributions from groundwater and

springs, mineralogy, and soil depth and chemistry have significant effects. This results in each stream and pond having a unique character determined by the configuration and components of its watershed.

f. Conclusions. Figures 28 through 30 do not show any relationship between acid loading events and stream pH. Possibly, a relationship would have been revealed if excess acid loading, instead of total acid loading, had been plotted. Excess acid loading is defined as that which causes precipitation to drop below the normal pH, which is variously defined as 5.6 to 5.4 (NED 1984). However, it appears that the project watersheds were able to handle the range of acid loadings that occurred in 1987 as there are no significant sharp, or even gradual, drops in pH recorded by the AWQM that clearly are not due to monitor error. A comparison with figures 13 through 27 shows that the peak acid loadings in 1987 were as high or higher than those that occurred in the years from 1982 through 1986. It should be noted that peak acid runoff events generally occur during snowmelt events (Buso, 1984; Klein, 1984; Ruby, 1988) at which times the AWQMs are in storage to protect them from freezing. should also be noted that the monitors collect data during the warmer months when biological generation of acid neutralizing capacity (ANC) is greatest. All of which means that, during the times in 1987 when the AWQMs were in place, the project watersheds as a whole were able to handle the acid loadings they received. How subwatersheds reacted during that time and what the watershed reactions were to high acid loadings when the biological ANC production was at a minimum are not known.

7. ACIDIFICATION TRENDS

a. Trends in Acid Rain Effects Reported in Recent Literature. Before examining data collected at NED projects for signs of trends in acidification, a literature search was performed. The purpose of this search was to learn what other researchers were finding about trends, and how they were measuring these trends.

A number of researchers are embarked on long term studies of the effects of acid precipitation; however, most of them have not been operating long enough to measure significant changes.

The longest record examined was by Taylor (1985) in a survey of the effects of acid rain on water supplies from New England through North Carolina. Using data collected by the Lawrence Experiment Station (LES) going back to 1887 and the Scituate Reservoir Laboratory going back to 1937, he looked for trends in alkalinity and pH over time in New England water supplies. Taylor had great faith in the quality of these data. Of 34 Massachusetts water supplies analyzed for

alkalinity at LES, 28 showed a downward trend of which 18 had slopes statistically different from zero at or better than the 0.05 level, and 6 had upward trends of which two were statistically significant.

Scituate Reservoir, which is the major water supply for Providence, Rhode Island, provides the most extensive pH and alkalinity data covering all seasons of the years in addition to being from the same sampling point. The slopes of plots of pH versus time and alkalinity versus time are both downward.

Taylor concluded that the decline of pH and alkalinity at Scituate Reservoir is consistent with an acid rain cause and effect hypothesis. The statistically significant decline of alkalinity in a majority of the Massachusetts supplies, their limited buffering capacity and the low pH of rainfall over the study area support such an hypothesis.

Taylor also found that acid rain has not brought about a deterioration of water quality such that EPA mean contaminant levels (MCL's) are exceeded. However, the aggressiveness of many of the waters combined with their low pH and alkalinity caused copper and lead levels in morning samples from many households to exceed these MCL's. Forty percent of the early morning samples, taken from areas served by the reservoirs examined, exceeded the MCL for copper of 1 mg/l and 5 percent exceeded the MCL of 0.05 mg/l for lead.

The "Interim Report on the Findings of the Massachusetts Acid Rain Research Program" (Godfrey et al. 1988) reported that in the 3 years between September 1983 and September 1985, samples of 401 Massachusetts lakes and streams showed that 214 surface waters improved slightly, 9 stayed the same, and 88 deteriorated. Acid loading during this period declined 50 percent. North central Massachusetts was found to be extremely sensitive to acid inputs.

In studies of the Quabbin Reservoir and its tributaries, Keller (1988) found evidence of increasing acidification in the fact that sulfate levels have nearly doubled since the 1950's, are now at 6 to 8 mg/l, and have replaced carbonate as the major ion. Keller also found evidence, in the complicated behavior of alkalinity levels in the reservoir, that the watershed was being acidified.

Low alkalinity at the Quabbin Reservoir occurs during both years of low precipitation and above normal precipitation (greater than I standard deviation). Reservoir volume is not a major factor in buffering the system: reservoir and tributary alkalinity is largely dependant on watershed acid neutralizing capacity (ANC).

Initially, higher ANC values, due likely to low flows and increased biological production, occurred during the months of June to August. However, from 1978 on, summertime alkalinity dropped sharply and was no longer distinguishable from spring and fall alkalinity. This suggests a possible reduction in micro flora ANC production within the river and soils of the watershed, a possible consequence of increased aluminum toxicity.

Alkalinity pulses occur at Quabbin, following episodes of low pH in the reservoir, in association with hardness and alkalinity peaks in the main tributaries. These pulses are due to loss of soluble ANC generating materials in the watershed and do not represent a true recovery. They appear to be a symptom of accelerated chemical leaching in the watershed due to increasing acidification.

Haines and Akielaszek (1983) conducted a survey of 226 headwater lakes and low order streams in the six New England states for indications of acidification. The waters selected had relatively little direct human disturbance, and were low in color thus eliminating those bodies of water which might be significantly acidified by organic acids.

Acidic (pH less than 5) surface waters occurred in every state. Approximately 8 percent of the waters surveyed had pH less than 5, and 29 percent had pH less than 6. The low pH waters tended to occur in clusters, although high pH waters frequently occurred in the same area. Waters with low alkalinity content were more common than low pH waters, and tended to occur in the same areas as the acidic waters. Approximately 24 percent of the waters had alkalinity concentrations of 20 micro-equivalents per liter (ueq/1) or less, 41 percent had concentrations of 100 ueq/1 or less, and 53 percent were 200 ueq/1 or less.

Calcite saturation index (CSI) results were similar to alkalinity, and CSI and alkalinity were highly correlated. Approximately 59% of the waters surveyed had CSI values greater than 3, and were classed as susceptible to acidification. This is the same conclusion reached based on alkalinity data. Specific conductance, an index of total ionic concentration, was correlated with alkalinity and could be used as a simple index of vulnerability to acidification. However, the coefficient of correlation was low.

Lakes and streams surveyed contained appreciable sulfate concentrations (80-120 ueq/1) that could not be attributed to marine aerosols. Concentrations were similar to those found in other areas where precipitation is similarly acidic, but were relatively uniform, and sulfate was not positively correlated with hydrogen ion. This lack of correlation may result because precipitation, and thus sulfate deposition, is chemically uniform over the region surveyed.

Historical pH and alkalinity data indicate that waters located in areas where buffering capacity is low have been acidified. Of the 95 lakes with usable historical pH data, 61 (64 percent) were lower in pH in this survey. Of 56 lakes for which historical alkalinity data were located, 39 (70 percent) were lower in the present survey. The average lake for which historical data were available increased in hydrogen ion content five-fold and decreased in alkalinity by 60 percent.

The relationship between pH and calcium content of surface waters (Henriksen 1979) was tested as an indicator of acidification. This model predicted that 57 percent of the waters surveyed had been acidified, a value in good agreement with that obtained from lakes for which historical water chemistry data were found. The model further predicted an average loss of about 50 ueq/l of alkalinity. Historical data, all from low alkalinity lakes, indicated a decline of about 100 ueq/l. Given the large range of chemical conditions encountered, this was considered to be reasonably good agreement.

Haines and Akielaszek concluded that a substantial portion of the headwater lakes and low order streams in New England are vulnerable to acidification, and that alkalinity is the best measure of vulnerability. Both historical water chemistry comparisons and acidification models indicate that the vulnerable lakes have declined in alkalinity and increased in hydrogen ion content, presumably as the result of atmospheric deposition of acid.

Rittmaster et al. (1988) found that 97 percent of the acid deposition load that fell on two tributaries to the Quabbin Reservoir was other than normal atmospheric carbondioxide. The weighted average pH in precipitation was 4.2 and the range was 3.6 to 5.0.

Batchelder et al. (1983) found that over 99 percent of the incoming hydrogen ions falling on Caldwell Creek watershed in central Massachusetts were not leaving the watershed in stream water but were apparently being stored in the biomass and soil components of the watershed by replacing previously adsorbed cations. Cation equivalents of sodium, potassium, calcium, and magnesium are leaving the watershed at a yearly rate which is six times greater than the rate at which they are introduced into the watershed through precipitation.

Van Breeman et al. (1984) identified and quantified proton fluxes in order to determine if the atmospheric inputs of acidic substances had a greater impact on soil acidification than the internal proton production of soils affected by changing land use. They calculated rates of acidic deposition and internal proton sources for a variety

of areas in the U.S. and Europe. They concluded that in the northeastern U.S. the atmospheric deposition of anthropogenically-derived acidic substances (mainly H^+ , SO_2 and NH_4^+) exceeds internally generated protons in soils with low rates of soil acidification and in many soils with intermediate rates. Soil acidification was defined as a decrease in ANC and is generally accomplished by removal of cationic components (such as CaO) from a mineral soil or, to a lesser extent, by addition of acidic components (such as SO_3). As a result, potentially toxic inorganic aluminium is released into the soil solution and H^+ and aluminium baseneutralizing capacity is transported to drainage waters.

The Water Quality Division of the Vermont Department of Water Resources and Environmental Engineering is embarked on a long term lake monitoring program for the effects of acid precipitation (Kellogg, 1984, 1985). After an initial assessment of nearly 200 lakes in 1979 that included virtually every water body in the state with a potential alkalinity of less than 250 ueq/1, 36 lakes were chosen for long term monitoring.

Initial analysis showed that acidification is suspected as causing the elimination of fish populations in two lakes. It was estimated that the fishery resources in Vermont have suffered little serious damage on the whole from acidification. Some of the survey lakes, however, showed potential for fisheries impact.

Rainfall data were also collected as part of this study. At four bulk deposition collection sites in Vermont, weighted average pH was 4.41 in 1983. In 1984, the weighted average pH at five sites was 4.38.

The most ambitious attempt to make regional estimates of the chemical status of lakes within a specific region or subregion is being performed by the U.S. Environmental Protection Agency in its Eastern Lake Survey (ELS) (Linthurst 1986). Part of the National Surface Water Survey, which is a contribution to the National Acid Precipitation. This study has not been in existence long enough to be able to show changes over time in the data collected. However, it can show existing conditions, and from that some trends can be inferred.

Data for the ELS was collected in the fall of 1984, when single samples were taken from 1,612 lakes from the Northeast, Upper Midwest, and Southeast. Chemical variables and physical attributes thought to influence or be influenced by surface water acidification were measured for each lake.

An initial analysis of the data collected by the ELS shows that most of the effects of acid precipitation are not felt most strongly in the Northeast. For example, the

subregions in the eastern U.S. that contain the largest proportion of acidic (ANC less than 0 ug/l) and low pH (less than 5.0) lakes are the Adirondacks, the Upper Peninsula of Michigan, and Florida.

Within the Northeast, the Adirondacks had the largest estimated percentage (11) of lakes with ANC less than 0 ueq/L, followed by Southern New England (5 percent), and the Poconos/Catskills (5 percent). Maine had the lowest percentage of acidic lakes (less than 1 percent).

Acidic lakes in the Northeast had higher concentrations of sulfate, calcium, and extractable aluminum than did acidic lakes in the Upper Midwest and Southeast. Sulfate concentrations in lakes were greatest in Florida and the southern portions of the Northeast. No linear relationship between lakewater sulfate and pH or ANC was evident in any region. High concentrations of sulfate were found at low and high pH values.

Sulfate concentrations were relatively high in the Northeast Region (median concentration (M) 115.4 ueq/1), being about twice that found in the Upper Midwest. Within the Northeast, sulfate concentrations were highest in the Poconos/Catskills (M=159.3 ueq/1) and Southern New England (M=141.1 ueq/1). The lowest sulfate values were observed in Maine (M=74.6 ueq/1).

Within the Northeast Region, Southern New England had the highest percentage of lakes with calcium concentrations less than 50 ueq/1 (10 percent). The Adirondacks contained the second highest percentage (8 percent) of low calcium lakes (less than 50 ueq/1).

Dissolved organic carbon (DOC) concentrations did not correlate with the distribution of acidic or low ANC lakes. In the Northeast, as in other regions, 80 percent of acidic lakes contained concentrations of DOC less than 5 mg/l. A positive relationship existed between pH and DOC. Those lakes with highest DOC concentrations were lakes with short hydraulic residence times and high ANC.

Anions were more useful than cations in characterizing differences in the relative importance of major ions among regions and subregions. In the Northeast, sulfate was the predominant anion in three of the subregions (Adirondacks, Poconos/Catskills, and Central New England). In Maine, bicarbonate ion concentrations exceeded sulfate. Chloride was the dominant anion in Southern New England. Organic anions, as indicated by anion deficit, were not the dominant anions in any subregion. Concentrations of organic anions were lowest in the Northeast.

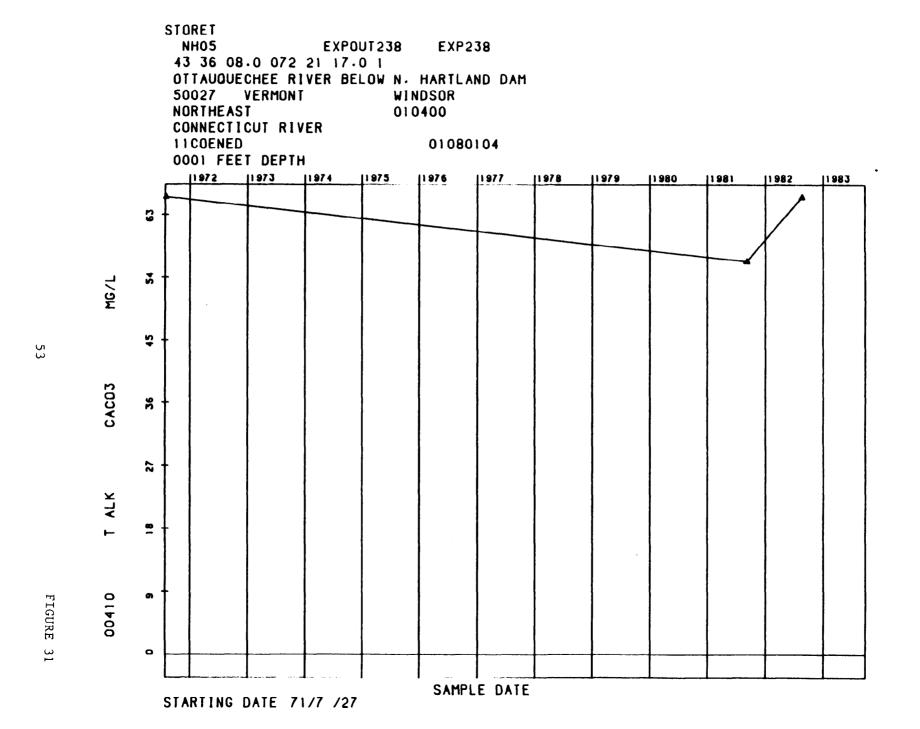
Using data collected by the Massachusetts Acid Rain Research Program, Ruby et al. (1988) found that the ELS data revealed good agreement for pH and alkalinity at sites sampled by both programs but that the EPA's statistical projections underestimate the actual numbers of low pH and low ANC lakes and ponds in Massachusetts.

b. Acidification Trends at NED Projects.

- (1) Alkalinity. Alkalinity measurements at NED projects were plotted over time to look for some indication of trends. Figure 31 is a typical plot. It basically shows that not enough alkalinity measurements were made to allow any meaningful trends to be observed. Appendix C contains the complete record of alkalinity plots over time.
- (2) Aluminum. Aluminum measurements at NED projects were plotted over time to look for some indication of trends. Figure 32 is a typical plot. It basically shows that not enough aluminum measurements were made to allow any meaningful trends to be observed. Appendix D contains the complete record of aluminum plots over time.
- (3) pH. Figures 33 through 52 are plots of pH versus time at a grab-sample-discharge and AWQM site for each of the ten projects. Also plotted on these figures is a best-fit linear regression line. Table 4 gives a summary of the periods of record, time spans, and slopes of the regression lines. The result is that 7 projects show an increasing pH, I project (Littleville Lake) shows an increase at one station and a decrease at the other, and only 2 projects (Barre Falls and Tully Lake) show a decreasing pH at both stations. Because of variables in the number of samples taken during the years of record and the months within each year that samples were taken, and because the AWQM data can include significant numbers of erroneous data points, the statistical significance of the exact slopes of the regression lines is small. What table 4 shows is that there have been no dramatic changes in the mean pH at NED projects over the period of record.

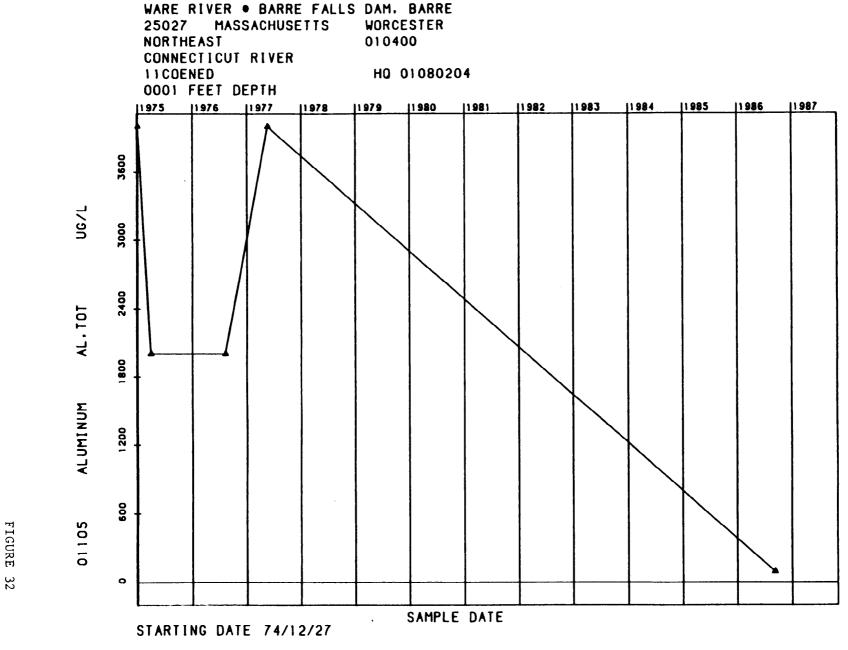
8. ALUMINUM

a. pH and Labile Aluminum. Initially, it was our intention to compare measured aluminum levels in NED project waters with the pH monitor record to look for some relationship between elevated aluminum levels and highly acidic precipitation or stream flow events. We expected that more acidic runoff would dissolve more aluminum from the soil, and dissolved aluminum levels would be inversely proportional to stream pH levels. To determine the extent to which such a simplified assumption was reasonable, we conducted a literature search on the relationship between runoff pH and aluminum levels.





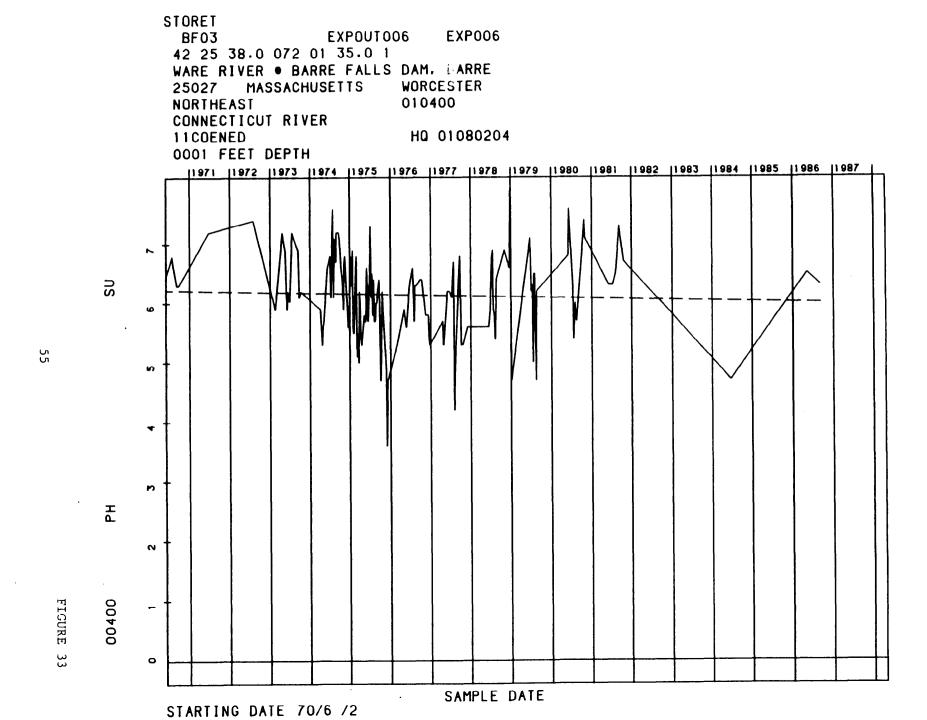
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EXP006

EXPOUTO06

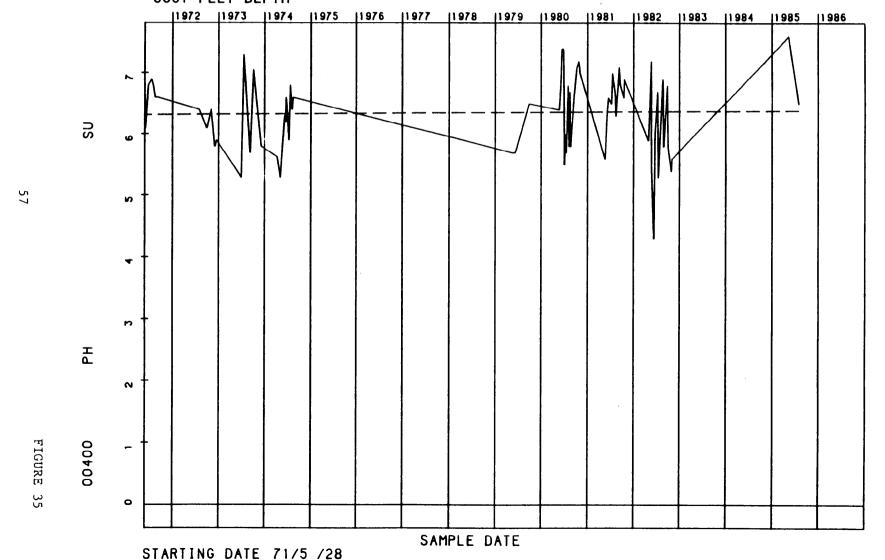
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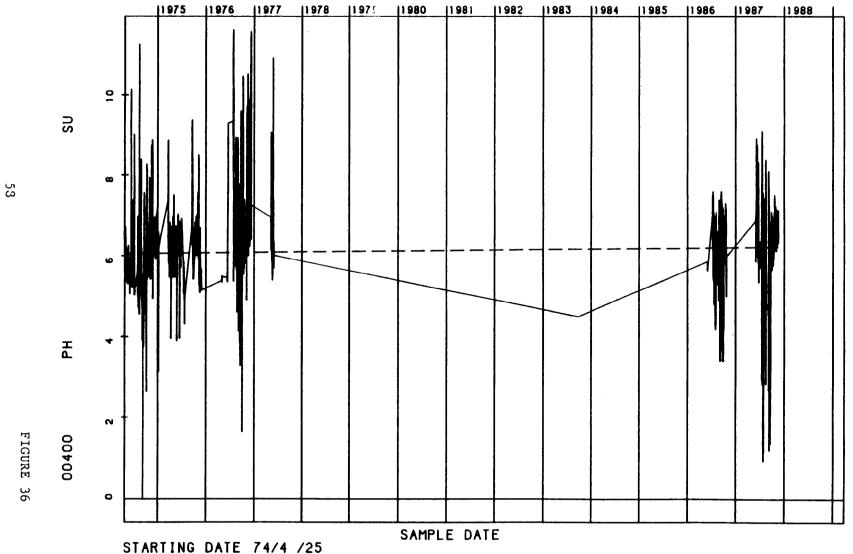
STORET BARR EXPWQM001 EXP001 42 25 38.0 072 01 36.0 1 WARE RIVER BELOW BARRE FALLS DAM, BARRE 25027 MASSACHUSETTS WORCESTER NORTHEAST 010491 CONNECTICUT RIVER 11 COENED HQ 01080204 0001 FEET DEPTH [1975 | 1976 | 1977 | 1978 | 1979 | 1980 | 1981 | 1982 | 1983 | 1984 | 1985 | 1986 | 1987 SU S Ī ~ 00400 FIGURE 34 0 SAMPLE DATE

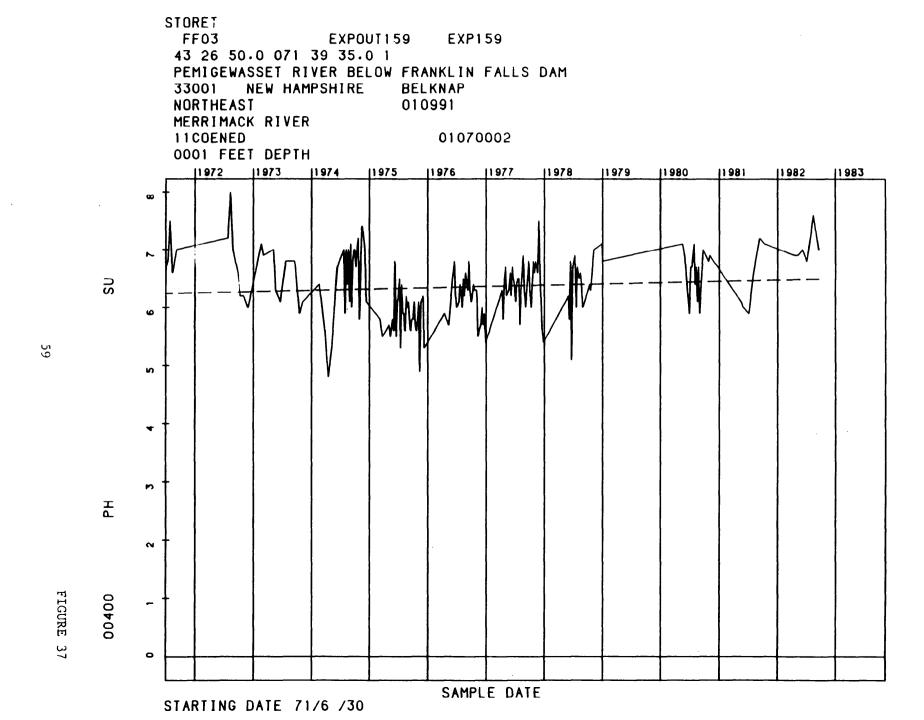
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42 37 57.0 072 07 30.0 1
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NORTHEAST 010400
CONNECTICUT RIVER
11COENED HQ 01080202009 0009.070 OFF
0001 FEET DEPTH



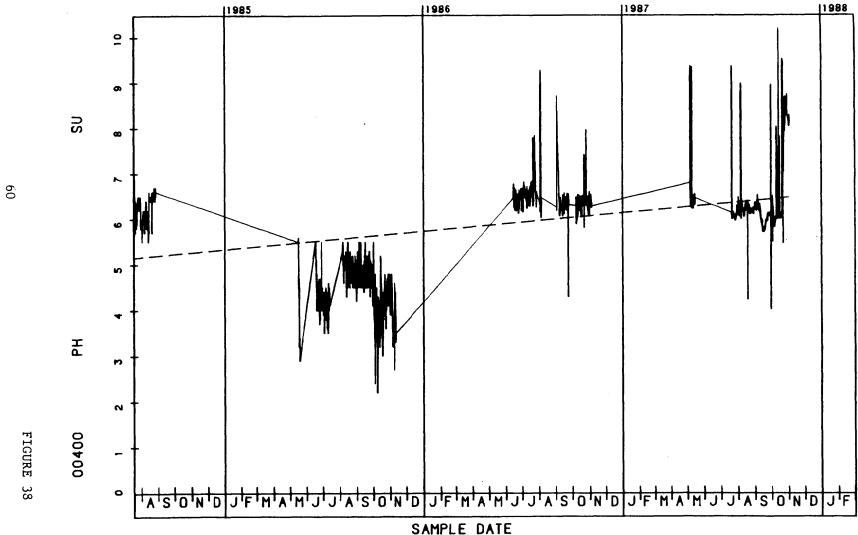
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0001 FEET DEPTH



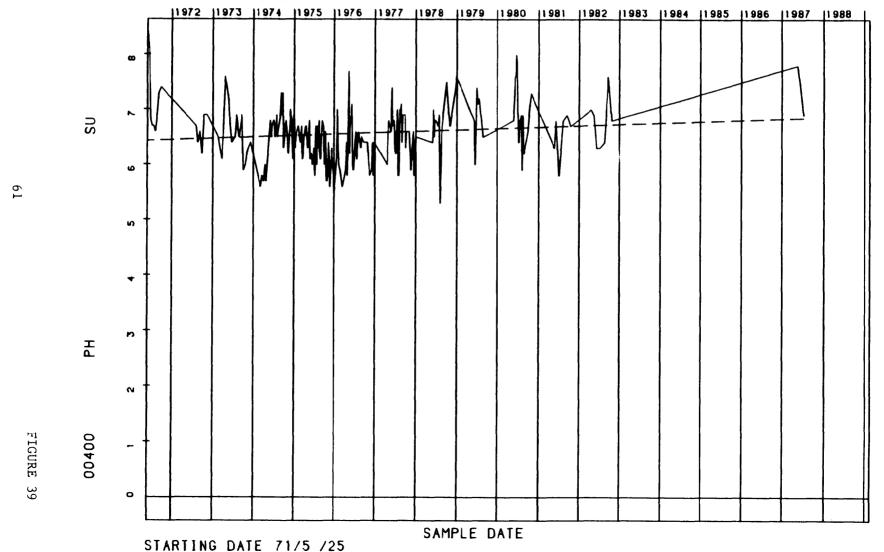


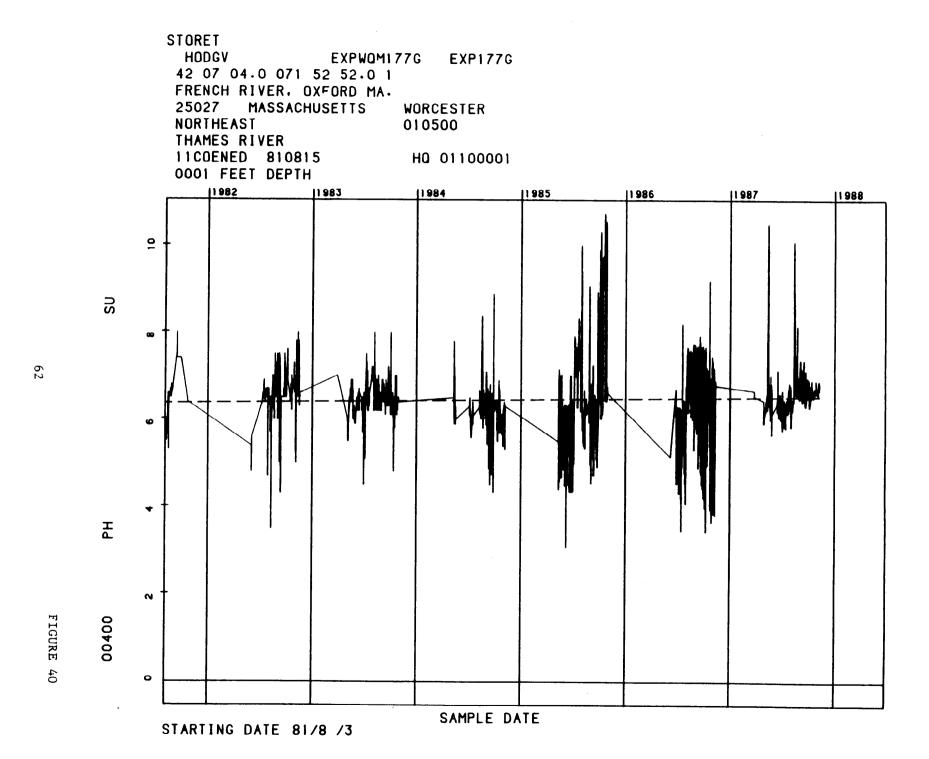
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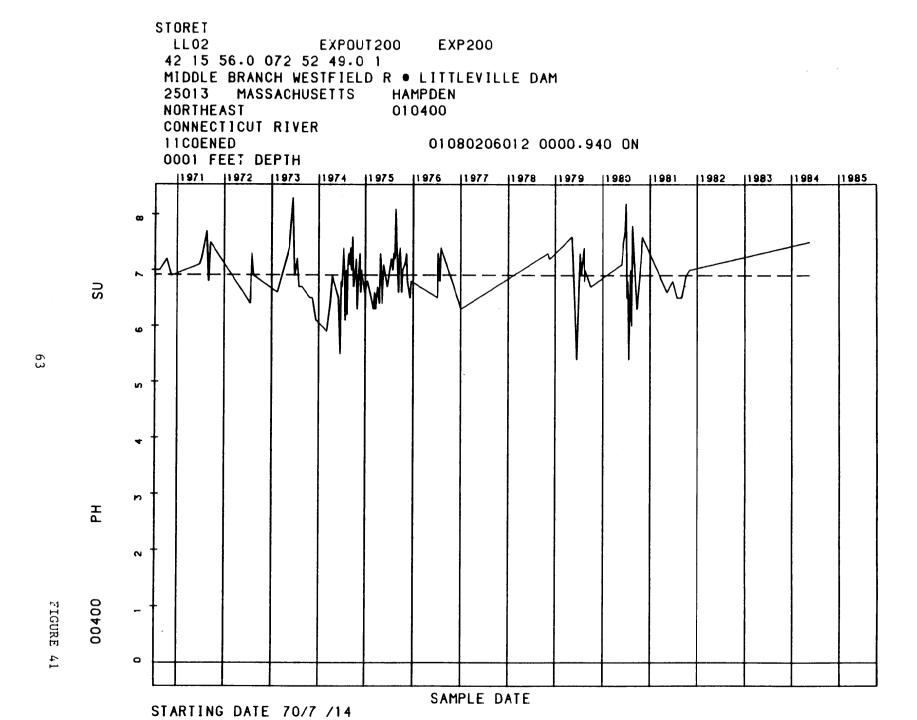
STARTING DATE 84/7 /18



STORET
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FRENCH RIVER BELOW HODGES VILLAGE DAM
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NORTHEAST 010500
THAMES RIVER
11 COENED HQ 01100001
0001 FEET DEPTH

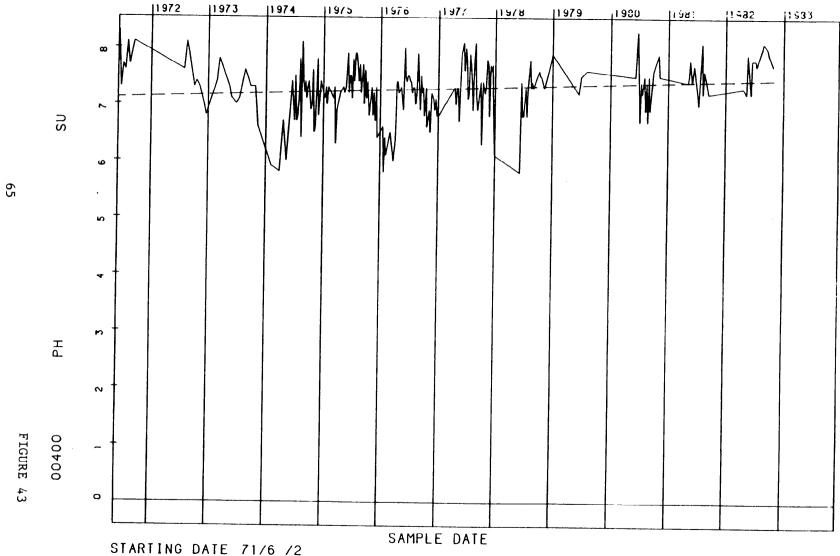




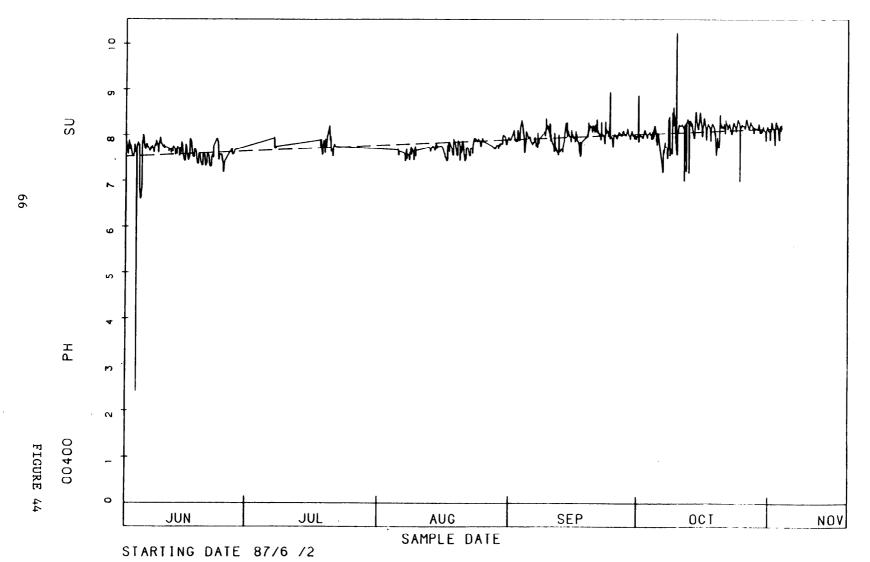


STUDY PROCESS

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50027 VERMONT WINDSOR
NORTHEAST 010400
CONNECTICUT RIVER
11COENED 01080104
0001 FEET DEPTH



STORET
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OTTAQUECHEE RIVER
50027 VERMONT WINDSOR
NORTHEAST MAJOR BASIN 010434
CONNECTICUT RIVER BASIN
11COENED 870627 01080106
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STORET

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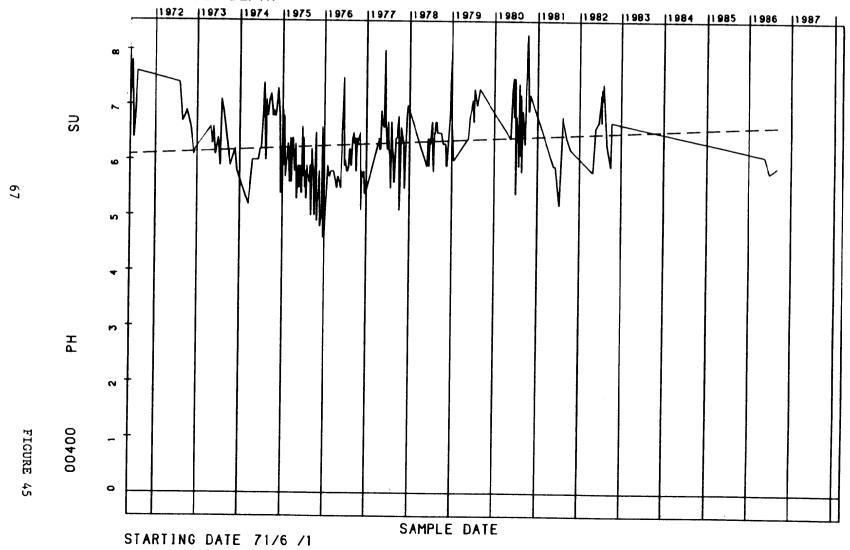
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NORTHEAST 010400

CONNECTICUT RIVER

11COENED 01080201

0001 FEET DEPTH



STORET

OTTE EXPWQM264 EXP264

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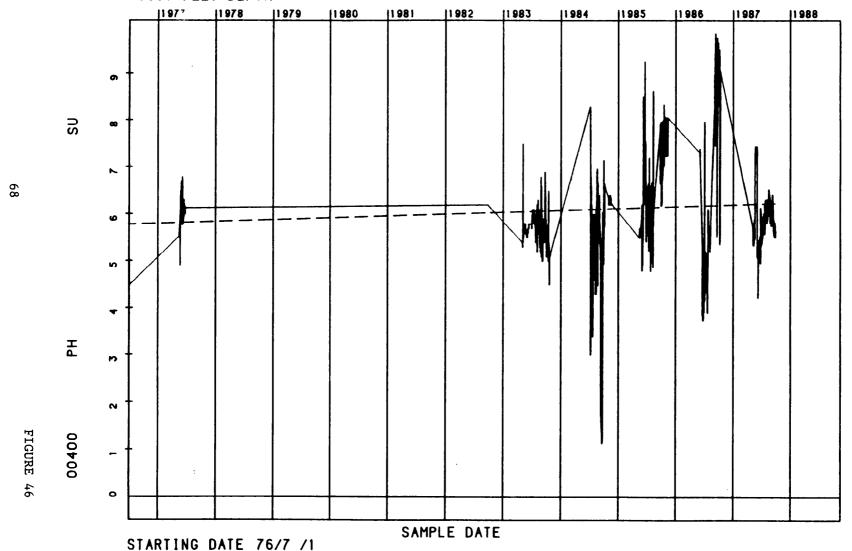
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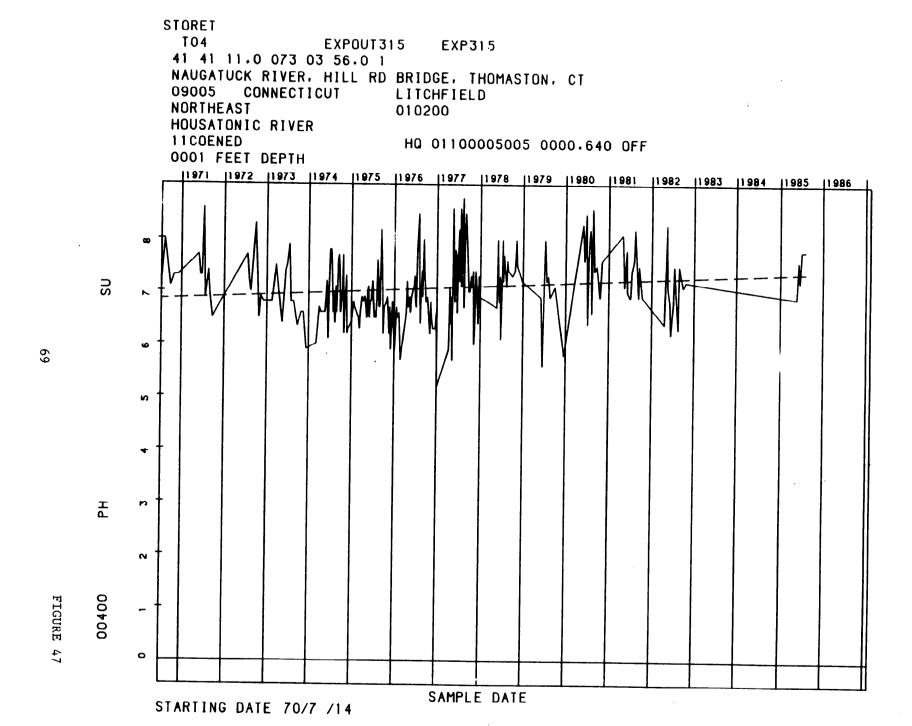
NORTHEAST 010400

CONNECTICUT RIVER

11COENED 760721 HQ 01080201

0001 FEET DEPTH





STORET THOM EXPWQM291A EXP291A 41 41 11.0 073 03 55.6 1 THOMASTON DAM IMPOUNDMENT, THOMASTON, CT. 09005 CONNECTICUT LITCHFIELD NORTHEAST 010200 HOUSATONIC RIVER 11COENED 810815 HQ 01100005005 0000.640 OFF 0001 FEET DEPTH 11983 1984 11985 11986 11987 11988 N SAMPLE DATE

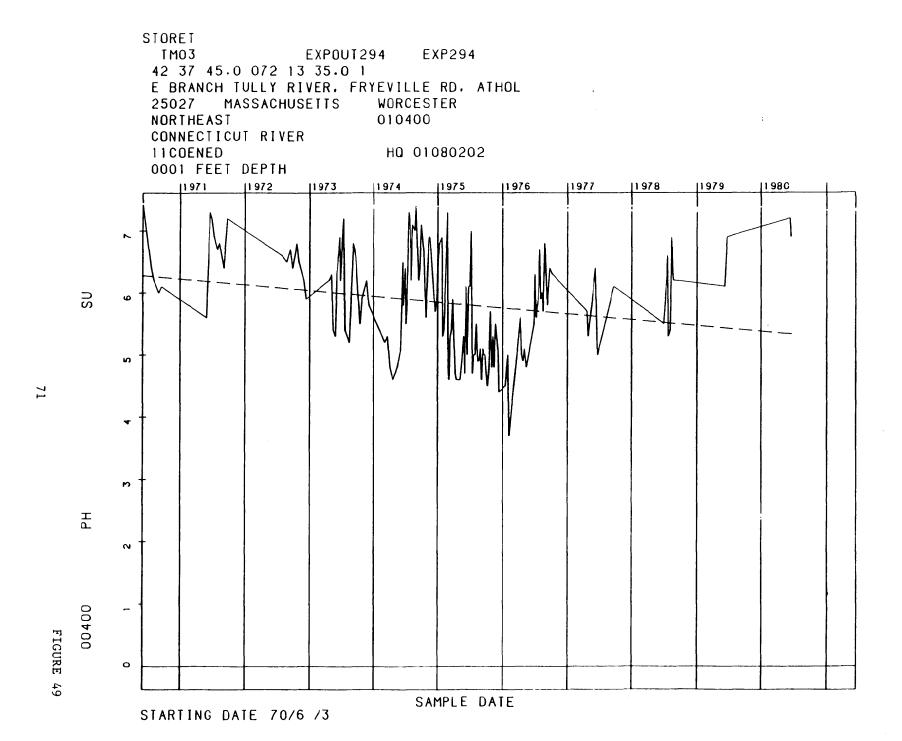
STARTING DATE 82/5 /6

SU

F H

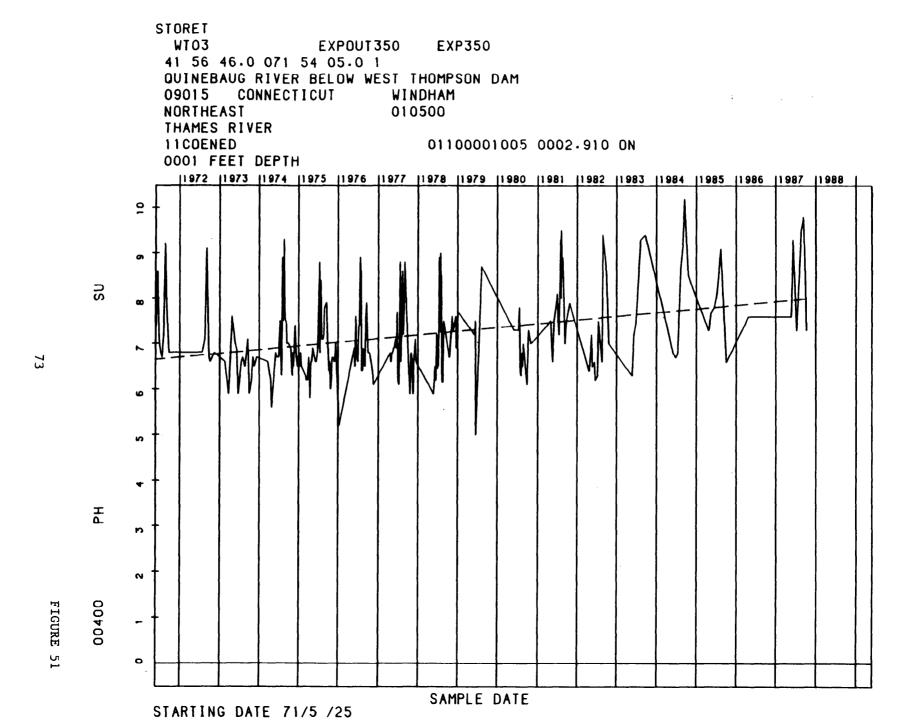
00400

FIGURE 48



SAMPLE DATE

STARTING DATE 82/5 /26



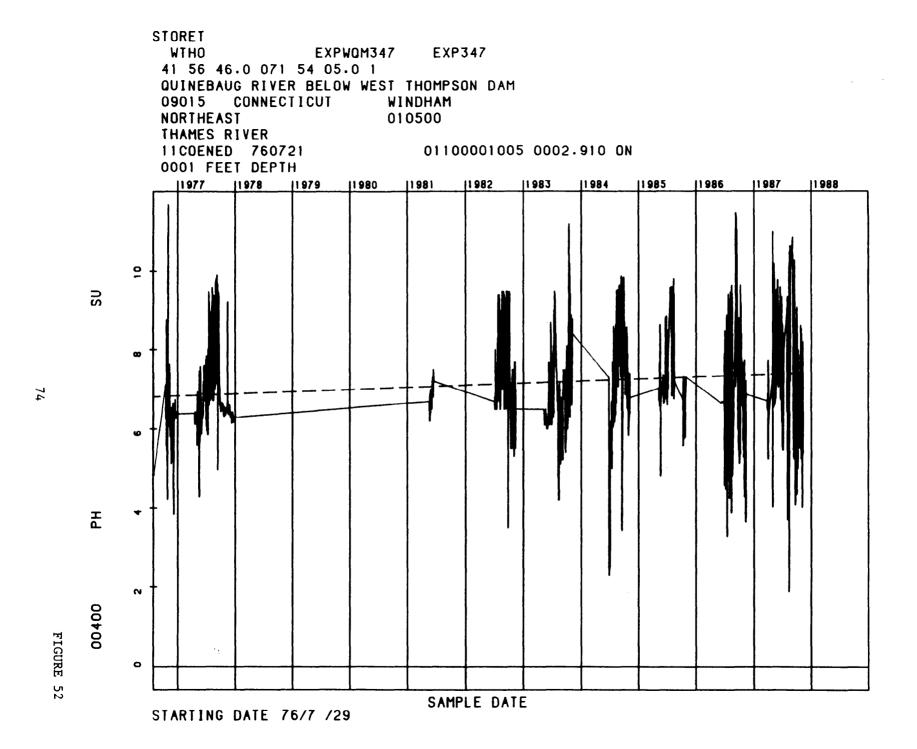


TABLE 4

ph TRENDS

Project	Station Identifier	Station Type	Period Record	Rate of Change (pH/year)	Time Span (years)	1984 Report Rate Change
Barre Falls	BF03 BARR	Grab AWQM	1970-86 1974-87	-0.0140 -0.0252	16.3 13.6	- -
Birch Hill	BHO5 BIRC	Grab AWQM	1971-85 1974-87	0.0053 0.0136	14.2	- -
Franklin Falls	FF03 FRANK	Grab AWQM	1971-82 1984-87	0.0221 0.3983	11.2	-
Hodges Village	HVO2	Grab AWQM	1971-87 1981-87	0.0261	16.1	0.0175 0.0844
Littleville	LL02 LITT	Grab AWQM	1970-84 1974-87		13.9 13.4	-0.0062 0.0901
North Hartland	NHO5	Grab AWQM	1971-82 1987	0.0298	11.4	- -
Otter Brook	OBO4 OTTE	Grab AWQM	1971-86 1977-87	0.0356 0.0113	15.3 10.4	0.0466 -0.0467
Thomaston	TO4 THOM	Grab AWQM	1970-85 1982-87	0.0350 0.3363	15.1 5.4	0.1908 0.0317
Tully	TM03 TULLY	Grab AWQM	1970-80 1982-87	-0.0945 -0.0699	10.0	- -
West Thompson	WT03 WTHO	Grab AWQM	1971-87 1976-87	0.0822 0.0534	16.4 11.3	0.0624 0.0681

That there would be a proportional relationship between runoff pH and aluminum levels was supported by the work of Johnson et al. (1980) who found in their studies of the Hubbard Brook Experimental Forest, in New Hampshire, that aluminum mobilization could be characterized as an equilibrium reaction between an aluminum trihydroxide $(Al(OH)_3)$ mineral and free aluminum (Al^3) activity.

Additional support for this theory came from the work of others including Hendry, Driscoll, Haines and Akielaszek, and Kellogg. Hendry (1984), in studies of softwater Florida lakes, found similar results for lakes less than pH 5.5. In these lakes, observed labile aluminum corresponded to aluminum predicted from kaolinite (the major aluminosilicate mineral in Florida soils) dissolution. Above pH 5.5, however, observed aluminum levels were roughly five times higher than predicted. Hendry theorized that this may have been due to analytical methods including organically complexed aluminum in the measurement of labile aluminum.

Driscoll (1980) studied three lakes in the southwestern Adirondacks and their tributaries. During seasonally low pH conditions, total aluminum levels increased dramatically, with increased levels of labile aluminum accounting for most of the change. Variations in organically chelated aluminum seemed to be independent of pH but were significantly correlated with total organic carbon measurements.

Haines and Akielaszek (1983) conducted a survey of 226 headwater lakes and low order streams in the six New England states. Selecting waters with little direct human disturbance, and that were low in color to eliminate the effects of organic acids, they found that correlations of aluminum with hydrogen ion content appeared to indicate that the thermodynamic equilibrium between hydrogen ion and aluminum controlled the aluminum concentration.

Initial analysis, of a long term lake monitoring program for the effects of acid precipitation in Vermont by Kellogg (1984, 1985) found that dissolved aluminum showed a negative correlation with pH and a positive correlation with color. In general, high dissolved aluminum concentrations were associated with highly colored lakes. Exceptions included two clear-water lakes which were devoid of fish.

However, temporal variations in the aluminum response to pH depressions found by Hooper and Shoemaker (1985) in their studies of Hubbard Brook indicated a more complicated aluminum mobilization mechanism than a mineral dissolution equilibrium. They found that aluminum concentrations were not in equilibrium with a readily formed mineral phase, as had been assumed, and that the increase in aluminum concentration due to episodic depressions in pH lessened during the snowmelt. They hypothesized that aluminum is

slowly converted into a labile form from the weathering of primary minerals and is accumulated in the soil. The first major flush (the midwinter thaw at Hubbard Brook) following an extended period of low flow would mobilize this more soluble form of aluminum. If this labile pool is leached out of the soil in the early stages of the melt by a large volume of water flowing through the watershed over a short period, there would be no elevation in aluminum above baseline levels during later acidic events.

Support for this theory could be found in the work of Henriksen et al. (1984). They documented a fish kill of Atlantic salmon due to acidic episodes in a western Norwegian river in controlled fish experiments combined with continuous monitoring of pH and daily water sampling. During a two-week period, four episodes with pH drops from 5.9 to 5.1 coincided with increased water flow due to rainfall and snow-melt, and were accompanied by dilution of calcium and substantial changes in aluminum speciation. The concentrations of inorganic monomeric Al increased from 0 to 50 ug/l during the pH drops. Henriksen speculated that the rapid changes in aluminum speciation could be due to dissolution of previously precipitated Al on the river bed by episodic flushing of the river from acidic snowmelt and storm events.

Studies by Rittmaster et al. (1988) of Quabbin Reservoir tributaries had ambiguous results concerning the method of formation of labile aluminum. In the Swift River, peak aluminum concentrations occurred under peak flow conditions. However, hydrogen ion concentration was directly proportional to discharge. Aluminum was highest and pH was lowest at the headwaters and decreased downstream. Thus it was not clear whether aluminum increased during high flows because the built-up reservoir of labile aluminum was being flushed from the soil, or because the lower pH occurring during higher flows dissolved more aluminum from the soil. At Fever Brook, the hydrogen ion concentration was not consistently correlated with flow. The highest pH was during periods of intermediate discharge in fall, winter and spring. Elevated aluminum was found in the headwaters only with snow melt and storm flows.

Budd et al. (1981) found, in the New Jersey Pine Barrens, that aluminum concentrations in streams was correlated with dissolved organic matter concentration suggesting that aluminum is transported as an organometallic complex.

It seems likely that the method of formation of dissolved aluminum and, therefore, the relation between aluminum levels and pH in either precipitation or stream flow depends on the characteristics of the watershed: its geology, hydrology, and flora. Geology determines the forms of aluminum-bearing and buffering minerals, hydrology determines

the residence and contact times of the water with these minerals, flora influence the organic acid contents of the waters. Each watershed would have to be studied separately, often on a very small scale, before the relationship between pH and aluminum could be established.

b. Aluminum Levels at Other Sites. In order to assess the significance of the levels of aluminum found at NED projects, it is important to know what levels are occurring in other sections of the Northeast, and if these levels are increasing.

Keller (1988) found evidence that aluminum levels in the Quabbin Reservoir and its tributaries are high and increasing. He estimated that 40-80 tons of aluminum may be moving from the watershed to the lake each year. Sediment cores showed a doubling or tripling of aluminum in the last 10-15 years, suggesting widespread watershed disturbance by excess mineral acids.

In the main body of the reservoir, aluminum levels are low. However, it is not unusual for aluminum to reach 0.2 to 0.3 mg/l in the thermocline in late summer for short periods. In August 1985, concentrations of 2.26 to 3.25 mg/l were measured within 10 meters of the bottom, 0.12 to 0.34 mg/l at the top of the thermocline, and 0.0 to 0.08 mg/l above the thermocline. This shows that significant amounts of aluminum can be remobilized from sediments.

Acid-impacted tributaries (pH 4.5-5.5) had aluminum levels of 0.2 to 0.4 mg/l while tributaries with pH 5.7-6.1 had 0.05-0.1 mg/l aluminum.

Sharpe et al. (1987) found in a survey of 61 headwater streams and their watersheds in Pennsylvania that 10 streams without fish had pH in the range of 4.29 to 5.96 with a mean of 4.80, and aluminum in the range of 15 to 1,000 with a mean of 512 ug/1.

Taylor (1985) in a survey of the effects of acid rain on water supplies from New England through North Carolina found thirty-four percent of the raw surface water supply samples had aluminum levels in excess of the 0.01 mg/l limit recommended by the American National Standards Institute for hemodialysis systems, and fourteen percent of raw ground water samples exceeded 0.1 mg/l aluminum.

Of the 226 waters surveyed by Haines and Akielaszek (1983, 13 had aluminum concentrations of 200 ug/l or more.

Miller (1984) found a median aluminum concentration in raw public water supplies in Region I (New England) of less than 0.014 ug/l with a maximum of 436 ug/l and 40 percent

greater than 14 ug/l. These levels made Region I aluminum levels fairly low compared to the rest of the country.

Dickson (1980) reported that total aluminum concentrations were highly pH dependent and found up to 700 ug/l at pH 4 in Swedish lakes; Driscoll (1980) found 400-800 ug/l in acidic Adirondack lakes and streams; and Herrman and Baron (1980) reported aluminum levels of 400-1,700 ug/l in southern Appalachian streams.

The Eastern Lakes Survey by the U.S. EPA of 1,612 lakes in the fall of 1984 (Linthurst, 1986) found that extractable aluminum concentrations were higher in lakes with lower pH values, and higher in the Northeast than in other regions. The largest estimated number of clear-water lakes (true color less than 30 standard color units) having extractable aluminum concentrations greater than 150 ug/l occurred in the Adirondacks. Few lakes in the Poconos/Catskills and Southern New England (1 percent) had extractable aluminum greater than 150 ug/l. No clear-water lakes sampled in Maine had extractable aluminum concentrations greater than 50 ug/l. In each region extractable aluminum concentrations were higher at lower pH values. The Northeast had the greatest increase in extractable aluminum with decreasing pH and Florida the least increase at low pH values.

c. Freshwater Criteria for Aluminum. A good criterion for protecting freshwater aquatic life from harmful levels of aluminum does not exist. The National Academy of Sciences-National Academy of Engineering warned in 1972 that, "Careful examination of toxicity problems should be made to protect aquatic life in situations where the presence of ionic aluminum is suspected. Aluminum may have considerably greater toxicity than has been assumed." This report suggested that anything greater than 0.1 mg/l of ionized aluminum would be deleterious to growth and survival of fish. However, the latest EPA water quality criteria (1986) still do not contain criteria for aluminum.

Part of the problem with setting a national criterion for aluminum in freshwater may be regional variations in its toxicity due to the presence of synergistic materials in the water. Also, the toxicity and solubility of aluminum is affected by pH to the point that toxic levels of aluminum are only found in waters with close to toxic levels of pH which further complicates the determination of just what is killing the fish. To complicate matters still further, although fish kills reported at pH's not regarded as toxic have been attributed to high levels of aluminum (Langdon, 1973) it has also been shown that aluminum can ameliorate the effects on fish of pH below 5 (Hutchinson et al., 1987). In order to try to determine what levels of aluminum at NED projects should be considered a threat to the aquatic life, a

compilation of recent research on toxic levels of aluminum in freshwaters is presented.

In his studies of tributaries to the Quabbin Reservoir, Keller (1988) found that rainbow trout in cages an acid-impacted tributaries (pH 4.5-5.5, total aluminum 0.2-0.4 mg/l) died in 2-4 days. Control fish in pH 5.7-6.1 with 0.05-0.1 mg/l aluminum did okay. In the Quabbin itself, smelt egg mortality was 18 to 43 percent with elevated aluminum levels in the range 0.1 to 0.2 mg/l.

Kostecki (1988) found that the hatching success of Rainbow Smelt was generally proportional to the pH level and inversely proportional to the aluminum ion level.

Sharpe et al. (1987) found in a survey of 61 headwater streams and their watersheds in Pennsylvania that 10 streams without fish had pH in the range of 4.29 to 5.96 with a mean of 4.80, and aluminum in the range of 15 to 1,000 with a mean of 512 ug/1. Of these 10 streams, Card Machine Run had a pH of 5.96 and an aluminum concentration of 15 ug/1. highest pH was 5.18 and the next lowest aluminum level was 400 ug/l. It would appear that Card Machine Run should have been capable of supporting trout. However, an earlier survey by Sharpe found a minimum pH of 4.5 and a maximum aluminum level of 700 ug/1 at this stream. In 33 streams which had fish, the pH ranged from 5.99 to 7.13 with a mean of 6.73, and the aluminum level ranged from 5 to 97 with a mean of 20 ug/1. At 6 streams with remnant fish populations the pH ranged from 5.49 to 7.06 with a mean of 6.19, and aluminum levels ranged from 18 to 300 with a mean of 88 ug/1. Because these streams were sampled only once the results are not in every case consistent. However, when the soil type in the watershed was considered, the watersheds with a minimum of limestone were all devoid of fish. This indicates that the streams would be sensitive to acid deposition events and may have had lethal pH and aluminum concentrations at some other time.

Gagen and Sharpe (1987) found that yearling brook trout experienced mortality during periods of low pH (to 4.53) and high dissolved aluminum concentration (greater than 0.2 mg/l) only if exposure exceeded one day. Acid runoff episodes with median aluminum concentrations as high as 0.3 mg/l were not fatal when duration was less than one day. Toxicity was attributed to severe sodium depletion caused by dissolved aluminum at pH levels which were otherwise nontoxic.

Hutchinson et al. (1987) found that joint action of hydrogen ions and inorganic aluminum produced mortality for fry of brook trout and lake trout, but aluminum toxicity required sublethal hydrogen ion stress. Aluminum increased survival time of eggs and fry of salmonoids during acutely lethal exposures at pH 3.5-4.2 and of adult sunfish at pH 3.5

SU. Reductions in the electrical and concentration potential for passive diffusion of sodium and chloride from blood to water was suggested as the mechanism affecting survival time during stressful conditions.

Driscoll et al. (1980) found that the form of aluminum in the water greatly influenced it toxicity. They measured aluminum in three forms: total aluminum, total monomeric aluminum, and non-labile monomeric aluminum. From these measurements, the total aluminum content of each sample could be subdivided into three fractions. Non-labile (organic) monomeric aluminum was measured directly and included organically chelated aluminum. Labile (inorganic) monomeric aluminum was the difference between total monomeric and nonlabile monomeric aluminum: this fraction includes free aluminum and aqueous inorganic complexes (fluoride, hydroxide, and sulphate). The third fraction, acid soluble aluminum was the total aluminum minus total monomeric aluminum and includes aluminum forms that require acid digestion before analysis (polymeric, colloidal, extremely stable organic and hydroxyl organic complexes).

Aluminum forms strong complexes with hydroxide, fluoride, sulphate and dissolved organic ligands. All these potential aluminum ligands are present in the dilute acidified waters of the study lakes and streams.

At pH 5.2, only 28 percent of the brook trout exposed to 0.42 mg/l total aluminum survived 14 days. With fluoride ligands added, the percentage of brook trout which survived a 0.50 mg/l aluminum concentration for 14 days rose to 45 percent. With citrate ligands added, the 14 day survival percentage for a 0.50 mg/l aluminum solution rose to 96 percent. Treatments with excess fluoride or citrate decreased the toxicity of aluminum solutions. Inorganic aluminum forms, therefore, seem to be the major species of concern with regard to aluminum toxicity in fish. As a result of reactions with hydroxide, aluminum toxicity to fish is pH-dependent.

Driscoll concludes that evaluation of aluminum speciation in acidified Adirondack water indicates organically complexed aluminum is the dominant form. As complexation of aluminum with organic ligands seems to eliminate its toxicity, measurement of total aluminum concentrations may lead to a substantial overestimate of the potential aluminum-induced toxicity. Additional studies of mortalities of white sucker fry supported this conclusion. The ameliorating effect of organic complexation on aluminum toxicity suggests that lake and streams with high organic carbon content may be suitable for successful fish production despite moderately low pH and high total aluminum levels.

Brown (1983) found that calcium decreased the toxicity of aluminum to brown trout yolk sac fry. In the absence of aluminum, mortalities at pH 4.5 occurred only with less than 0.5 mg/l calcium; with 250 ug/l aluminum, survival was very low at 0.5 mg/l calcium but had almost complete survival at 2 mg/l calcium; with 500 ug/l aluminum there was complete mortality at 0.5 mg/l calcium and significant mortalities at higher calcium concentrations. There was a tendency for higher pH to be more toxic especially in solutions containing 500 ug/l aluminum. Overall, the most striking differences were in the survival times between solutions containing 0.5 mg/l or less calcium and 1 mg/l or more.

Burton (1983) found that the presence of organic matter strongly reduced the toxicity of aluminum and also slightly reduced the toxicity of low pH. He concluded that the threshold for effects was between pH 5 and pH 4 and between 250 and 500 ug/l aluminum.

Witters (1986) exposed Rainbow trout, acclimated to low environmental calcium (138 ueq/1) to either acid water (pH 4.1) or acid water with aluminium (350 ug/1) for 3.5 hours. The exposure to aluminum in acid water provoked a massive whole body ion loss of sodium, chloride and potassium which was twice as high as in fish exposed to acid water. The presence of higher ambient Ca-levels (190 ueq/1) had no moderating effect on the toxicity of Al to the ion balance.

Skogheim (1984) investigated a fish kill in the River Ogna, in Norway. During a period in August 1982 the water in the main river was of good quality (pH 6.0, labile Al 13 ug/1). However, water flow in the main river decreased and acid, aluminium-rich water from a hydroelectric power plant strongly influenced the water quality (pH 5.17-5.54, labile Al 109-133 ug/1). During a period of about 35 hours more than 50 fish with weights of 3 to 10 Kg were found dead or dying in the river. Blood from dying salmon showed mean plasma-chloride levels of 110 meq/1, indicating significant loss of plasma-ions, This episode indicates high sensitivity of migrating spawners of salmon to acid water over-saturated with aluminium

Gunn (1984) in studies of lake trout sac fry in incubators at an Ontario spawning site during the spring snowmelt, found that most sac fry could tolerate pH less than 5.0 and 40-50 ug/l aluminum for at least 5 days. However, substantially higher concentrations of inorganic aluminum (about 80 ug/l) were found in the interstitial waters of the spawning rubble then in the overlying waters. Consequently, conventional open-water sampling programs and field and laboratory bioasseys may test organisms in less toxic environments than they are exposed to in their actual environments.

Leivestad et al. (1987) studied the mortality and stress indicators in Atlantic salmon using varying pH and aluminum levels. They found that failure in ionic regulation is the primary cause for mortality. Specifically, gill Na-K-ATP-ase activity is reduced at toxic aluminum levels. Thus it is "labile inorganic", i.e. "ion-exchangeable" aluminium rather than supersaturated precipitating solutions that are the main killers of fish in acidified fresh water.

d. Aluminum Effects on Terrestrial Flora. Some researchers have found evidence that labile aluminum levels may be occurring in harmful levels in New England soils. Keller (1988), in his studies of the Quabbin Reservoir, speculated that decreased summertime alkalinity values after 1978 were caused by reductions in micro flora alkalinity production within the river and soils of the watershed due to increased aluminum toxicity. Analysis of tree cores from white pines in Quabbin watershed showed an increase in aluminum and vanadium after 1962.

Klein (1984) found in studies of Vermont soils on Camels Hump Mountain that aluminum, particularly in soil solutions from the upper elevations is present in concentration known to be phytotoxic to seedlings of forest trees and to ground-cover plants. In the spring, cadmium, lead and zinc were also present in concentrations close to being phytotoxic.

e. Aluminum at NED Projects. Table 5 gives a summary of mean, minimum, and maximum aluminum levels measured at ten NED projects. These measurements are of total aluminum which includes organically complexed aluminum which has a very low toxicity. Consequently, it is difficult to accurately describe the problems, if any, caused by aluminum levels at NED projects. On the most basic level, there are no reports of fish kills or chronic problems with establishing resident fish populations which would indicate that aluminum toxicity is a problem at any NED projects. On the other hand, the mean aluminum levels at most of the ten NED projects is greater than the 100 ug/l level which appears to be the threshold level for aluminum toxicity problems to occur.

In the absence of other measurements, color levels can be used to estimate dissolved organic carbon levels which can, in turn, be used to estimate the fraction of total aluminum which is likely to be chelated. Table 6 lists the ten projects in descending order of color concentration. Tully Lake, and Birch Hill and Barre Falls Dams have the highest color levels; and Franklin Falls and Thomaston Dams, and Littleville and North Hartland Lakes have the lowest.

Of the four projects in table 5 with the highest aluminum levels, two of the projects - Tully Lake and Birch Hill Dam - have the highest color levels. West Thompson Lake has only moderate levels of true color, but has very heavy

TABLE 5

Aluminum Levels
(ug/l)

Project	Mean	Minimum	Maximum
Barre Falls Dam	108	90	132
Birch Hill Dam	403	165	730
Franklin Falls Dam	208	10	2,000
Hodges Village Dam	89	24	140
Littleville Lake	80	30	200
North Hartland Lake	162	29	460
Otter Brook Lake	119	70	230
Thomaston Dam	94	10	400
Tully Lake	172	7	395
West Thompson Lake	350	0	5,850
Overall	178	0	5,850

TABLE 6

Color Levels
(Pt-Co Units)

			% Greater than
Project	Median	Maximum	25 Pt-Co Units
Barre Falls Dam	90	205	100
Birch Hill Dam	100	1100	99
Franklin Falls Dam	2 2	45	3 2
Hodges Village Dam	61	100	8 5
Littleville Lake	15	70	23
Otter Brook Lake	46	95	8 5
North Hartland Lake	15	35	17
Thomaston Dam	2 1	160	33
Tully Lake	105	200	100
West Thompson Lake	60	250	95

algae blooms which result in high levels of dissolved organic carbon. That leaves Franklin Falls Dam and the Pemigewasset River as the most likely to have high levels of dissolved aluminum which could be harmful to aquatic life. Additional measurements of labile and organically-bound aluminum would be required to confirm this.

Mean aluminum levels at NED projects appear to be somewhat higher than levels found by other researchers studying New England waters. With an overall mean of 178 ug/1, aluminum levels at NED projects were higher than Taylor (1985) found in water supplies from New England through North Carolina, Miller (1984) found in public water supplies in New England, or that the ELS found in New England lakes. To some extent this is due to the more colored nature of NED waters as the other studies tended to exclude highly colored waters. Additional aluminum measurements including labile and chelated aluminum will be required to determine the extent to which apparently high aluminum levels at NED projects are due to the inclusion of organically-bound aluminum.

9. RANKING OF PROJECTS BY DEGREE OF ACIDIFICATION

- a. <u>Introduction</u>. The susceptibility of NED projects to the effects of acid precipitation can be measured in a number of ways, none of them exact. In this report we have ranked projects by their mean aluminum concentration, mean alkalinity, mean calcite saturation index, and Van Slyke buffer values.
- Aluminum. Table 7 gives a ranking of the ten NED projects involved in this acid rain study by mean aluminum concentration. Projects are listed in order of increasing aluminum concentration on the assumption that acidified watersheds have higher levels of aluminum in their runoff. This is only a crude measure of the comparative degree of acidification. For any given watershed, it is very likely that increasing acidification will result in higher aluminum levels in the overall runoff. However, it is very difficult to compare two watersheds, particularly when total aluminum is being measured. For example, if one watershed has greater amounts of dissolved organic carbon in its waters, the aluminum is likely to be in a chelated form resulting in higher levels of aluminum than would normally remain in solution at the pH of the water. Also, organically-bound aluminum is much less harmful than dissolved aluminum. It is for these reasons that mean aluminum concentration is judged a crude measure of the degree of acidification.
- c. <u>CSI</u>. Calcite saturation index (CSI), the logarithm of the degree of saturation with respect to CaCO₃ (Kramer 1976), can be a useful indicator of the pH-alkalinity relationship. CSI is defined as the sum of the negative log of the calcium concentration in moles per liter plus the

TABLE 7

Ranking of Projects by Aluminum Concentraion

Rank	Project	$(\frac{\text{Mean}}{\text{ug}/1})$
1	Littleville Lake	80
2	Hodges Village Dam	89
3	Thomaston Dam	94
4	Barre Falls Dam	108
5	Otter Brook Lake	119
6	North Hartland Lake	162
7	Tully Lake	172
8	Franklin Falls Dam	208
9	West Thompson Lake	350
10	Birch Hill Dam	403

TABLE 8

Ranking of Projects by Calcite Saturation Index

Rank*	Project	Mean	<u>Minimum</u>	Maximum
1	North Hartland Lake	0.0	0.0	0.0
2	Thomaston Dam	1.7	0.0	3.3
3	Littleville Lake	2.8	0.4	4.2
4	West Thompson Lake	2.8	2.4	3.2
5	Hodges Village Dam	3.1	2.8	3.5
6	Tully Lake	3.3	3.2	3.4
7	Otter Brook Lake	3.5	3.2	3.7
8	Franklin Falls Dam	3.8	1.6	5.0
9	Birch Hill Dam	3.9	3.9	4.0
10	Barre Falls Dam	4.4	4.2	4.7

^{*}An increasing rank indicates a decreasing stability with respect to acid loading.

negative log of the alkalinity in equivalents per liter, plus the log of the hydrogen ion concentration plus the negative log of the calcium carbonate equilibrium constant (which for natural waters can be taken as "2"). If a body of water is saturated, with respect to CaCO₃, the CSI equals zero; if supersaturated, the CSI is less than zero, and if undersaturated, the CSI is greater than zero. A CSI less than or equal to 3 indicates a body of water that is generally stable relative to acid precipitation (Haines and Akielaszek 1983). Bodies of water with a CSI from 4-6 are unstable relative to acid loading and are typically non-productive (Kramer 1976).

Table 8 lists the ten projects by increasing CSI. By this measure, North Hartland Lake, Thomaston Dam, and West Thompson and Littleville Lakes are in good shape; and Barre Falls Dam may be affected by acid precipitation to the point that the biological productivity of its waters may be affected. The remaining five projects are in a borderline region.

d. <u>Buffer Values</u>. Faust et al. (1981, 1983) showed that although alkalinity is often referred to as a measure of the buffering capacity of water, this is incorrect and misleading. Total alkalinity is a measure of the capacity of a water to neutralize a specific quantity of an acid. Buffer capacity, or buffer value as originally defined by Van Slyke (1922), is the relation between the increment of a strong acid (or a strong base) that causes an incremental change in the pH value of the water. A buffer value (M) of 1 indicates that a 1 liter solution requires 1 gram equivalent of strong acid to cause a unit change in pH value.

Alkalinity and pH values, considered individually, cannot give an accurate assessment of the impact of acid deposition on a natural water. Rather, it is necessary to consider pH and alkalinity into the B concept in order to assess and calculate accurately the capacity of a natural water to resist the impact of acid deposition.

One way to think of the significance of Van Slyke's buffer values is to consider two waters, X and Y, with the same alkalinity, say 6.0 mg/l, but different pH, say 7.0 and 5.5, respectively. It would require an addition of 7.8 mg/l of sulfuric acid to bring either water to an alkalinity titration end point of pH 4.5. However, the average pH drop per mg/l of acid added is 0.32 for water X, but only 0.13 for water Y. This illustrates how water Y, although it has a lower pH, is better protected against small changes in pH than is water X.

Table 9 lists the ten projects in order of increasing Van Slyke's buffer values. The most sensitive waters were

TABLE 9

Ranking of Projects by Buffer Values

Rank	Project	Buffer Va <u>Mean</u>	lues (x 1 <u>Min</u>	0 exp-5) <u>Max</u>
1	Birch Hill Dam	-22.6	-49.7	-7.32
2	Thomaston Dam	-20.8	-83.2	-0.77
3	Hodges Village Dam	-16.8	-39.1	-1.71
4	West Thompson Lake	-15.0	-44.2	-0.75
5	North Hartland Lake	-13.0	-31.2	-5.12
6	Barre Falls Dam	-11.2	-15.6	-6.81
7	Otter Brook Lake	-8.6	-15.1	-1.21
8	Franklin Falls Dam	- 7.5	-18	-1.04
9	Littleville Lake	-7.0	-10.7	-4.03
10	Tully Lake	-5.4	-21.6	-0.13

^{*} An increasing rank indicates a decreasing ability to buffer the effects of acid inputs.

TABLE 10

Ranking of Projects by Alkalinity

Rank	Project	Mean	Alkalinity mg/l as CaCO3 <u>Min</u>	Max
1	Birch Hill Dam	129.5	3	470
2	North Hartland Lake	79.2	5 5	133
3	Hodges Village Dam	37.0	4	200
4	Barre Falls Dam	32.3	2	90
5	Thomaston Dam	31.3	1	120
6	West Thompson Lake	30.7	4	349
7	Littleville Lake	25.3	6	110
8	Otter Brook Lake	14.6	0.5	163
9	Franklin Falls Dam	5.3	3	11
10	Tully Lake	1.8	0	6

considered (by Faust, 1983) those whose B values were greater than -10×10 to the minus 5.

e. Alkalinity. Simply comparing mean alkalinity levels is a good method of comparing the degree of acidification and susceptibility to further acidification of a watershed. CSI and Van Slyke's buffer value calculations include alkalinity measurements. Van Slyke's buffer calculations are better for determining the resistance of the water to further small changes in pH, but are no improvement over simple alkalinity measurements in measuring the resistance to large changes in pH. Haines and Akielaszek (1983) found that CSI results were similar to alkalinity, and CSI and alkalinity were highly correlated.

Table 10 gives a ranking of the ten projects by mean alkalinity values. Birch Hill Dam and North Hartland Lake come out as best protected from acidification and Tully Lake is the most susceptible.

f. Summary. Table 11 combines the previous four tables to give a summary of the ranking of the projects by alkalinity, CSI, buffer values, and aluminum concentration. An overall ranking and the ranking from the 1984 report are also included. The overall ranking was computed by averaging the results of the aluminum, CSI, buffer value, and alkalinity rankings with the aluminum ranking weighted half as much as the others. Because the 1984 report looked at only 7 projects of which only 6 are included in this report, the 1984 rankings were multiplied by 1.4 to make them comparable.

North Hartland Lake is the best protected from the effects of acidification and Tully Lake is the most susceptible. The other projects are in-between in somewhat uncertain order.

10. SUMMARY AND CONCLUSIONS

During the 17 years that the Corps has been measuring water quality, the mean pH at these projects does not appear to have changed significantly. The acid load to the watersheds appears to have stabilized and biological acid neutralizing capacity (ANC) production plus the weathering of soils are producing a rough equilibrium. While no dramatic effects from acid precipitation on NED projects were noted in this report, levels of alkalinity, calcite saturation indices, and Van Slyke buffer values at some projects indicate minimal resistance to further watershed acidification. As shown by Keller's (1988) studies of the Quabbin Reservoir, acidification of a watershed can lead to increases in stream alkalinity which can make conditions appear to be better than they actually are. This is because these increases are not sustainable but represent an

TABLE 11

Overall Ranking of Projects*

Project	Alkalinity	CSI	Buffer <u>Value</u>	Aluminum	Overall Ranking	1984 <u>Ranking</u>
North Hartland Lake	2	1	5	6	1	
Hodges Village Dam	3	5	3	2	2	7
Thomaston Dam	5	2	2	3	3	4
Birch Hill Dam	1	9	1	10	4	
West Thompson Lake	6	3	4	9	5	3
Barre Falls Dam	4	10	6	4	6	
Littleville Lake	7	4	9	1	7	6
Otter Brook Lake	8	7	7	5	8	9
Franklin Falls Dam	9	8	8	8	9	
Tully Lake	10	6	10	7	10	10

^{*} An increasing rank indicates a decreasing ability to withstand the effects of acid inputs.

accelerated leaching of ANC materials from the watershed. Consequently, while there are no dramatic signs of acid rain affecting NED projects, there are subtle indications that watershed acidification is occurring and should continue to be monitored.

There is no evidence that storms with heavy acid loads produce lowered pH levels in streams; however, this may be due to a lack of AWQM records with the proper combination of duration and reliability. It should also be noted that the peak acid-loading events to streams occur during snowmelt when the AWQMs are not deployed and little grab-sample data are collected.

A review of the literature shows that no good criterion to protect sensitive aquatic life from hazardous levels of aluminum have yet been developed. This is in part because of the complicated relationship between aluminum and pH. Although aluminum is most toxic to fish at low pH, at very low pH aluminum can actually increase the survival time. Also, the form of aluminum is very important since dissolved aluminum is most toxic and organically-bound aluminum is only slightly toxic. Aluminum levels at NED projects are near. and in some cases above, the levels that have been found toxic by researchers at other sites. Aluminum levels appear to be higher at NED projects than other researchers are finding for New England sites in general. Additional measurements to determine the form of aluminum will be needed to determine the magnitude of the threat to sensitive aquatic life at NED projects.

Kriging appears to be a good means for combining precipitation data from a variety of sources and plotting total acid load throughout the year. These plots show that the acid load tends to be greatest during the summer, and that there is no obvious relationship between acid loading and pH levels in the runoff; however, only a limited number of plots were created.

Projects were ranked as to their present acidification and susceptibility to further acidification by aluminum concentration, alkalinity concentration, calcite saturation index, and Van Slyke's buffer values. The results show North Hartland Lake is the best protected from and Tully Lake is the most susceptible to the effects of further acidification. The other projects are in between with no definite order amongst them.

Further research needs to be done on improving the quality of the data collected by NED's automatic water quality monitors and on determining the forms of aluminum in the waters of NED projects. A baseline of alkalinity and aluminum data needs to be collected to permit an evaluation of trends in these parameters.

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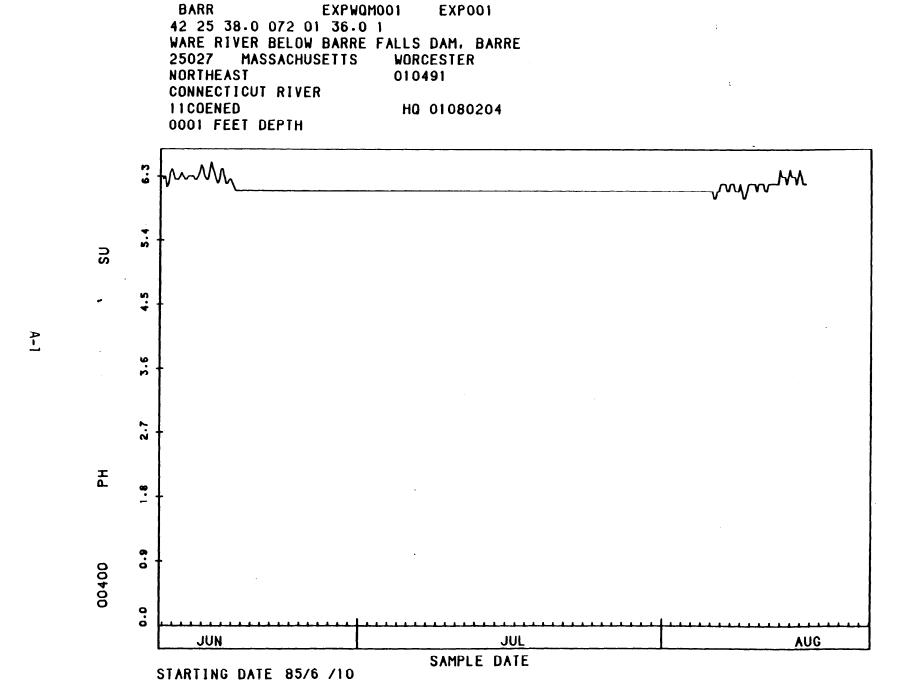
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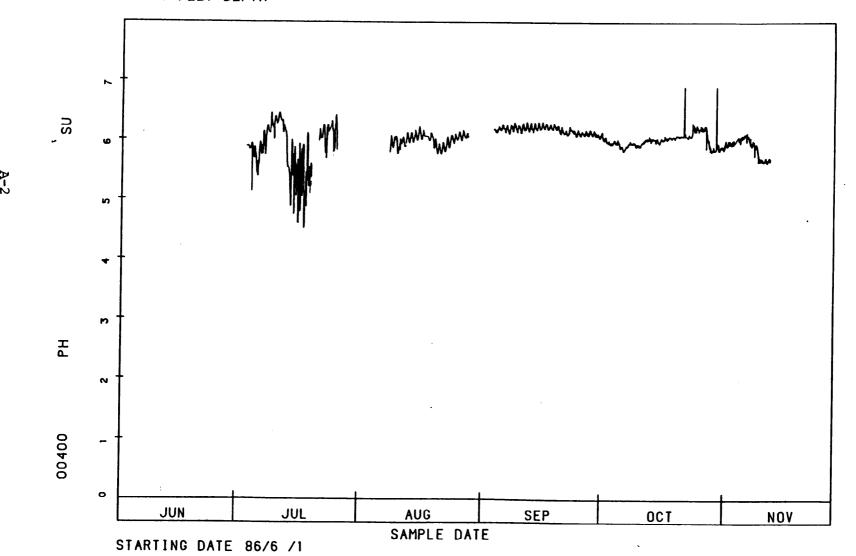
APPENDIX A

Automatic Water Quality Monitor Plots $pH \ \ Records$

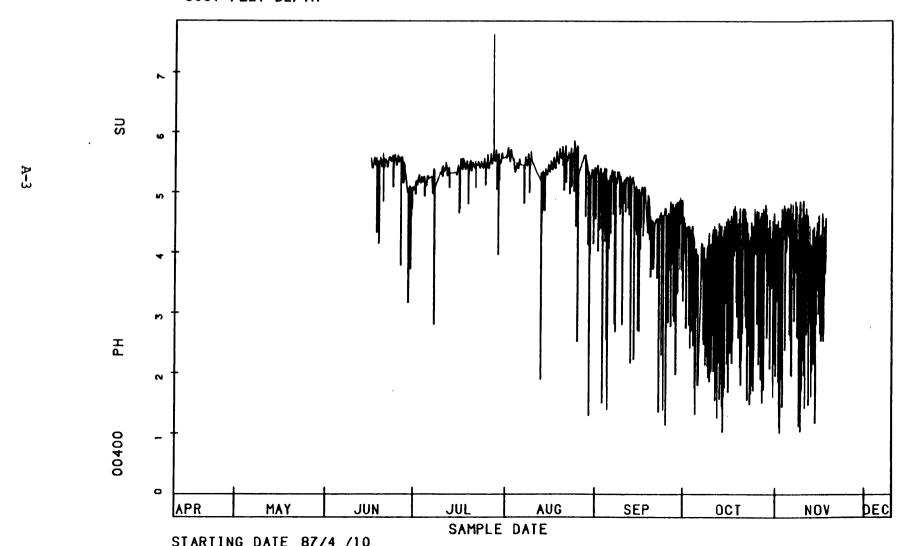


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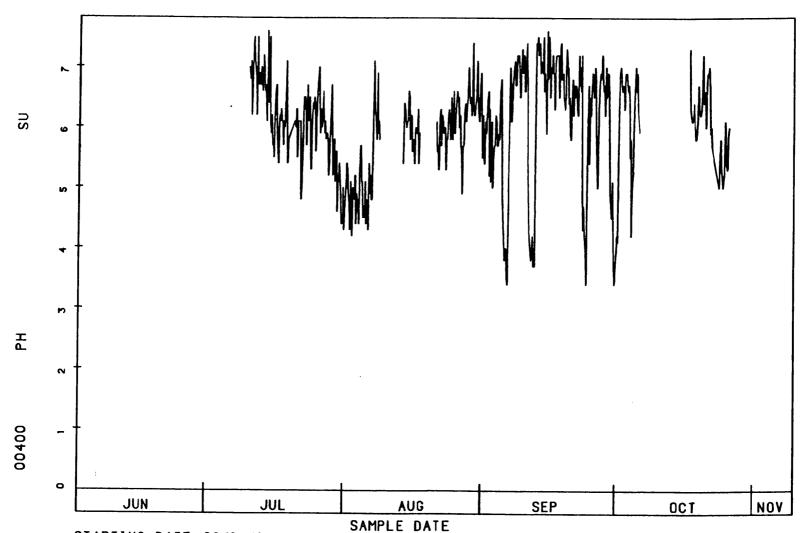
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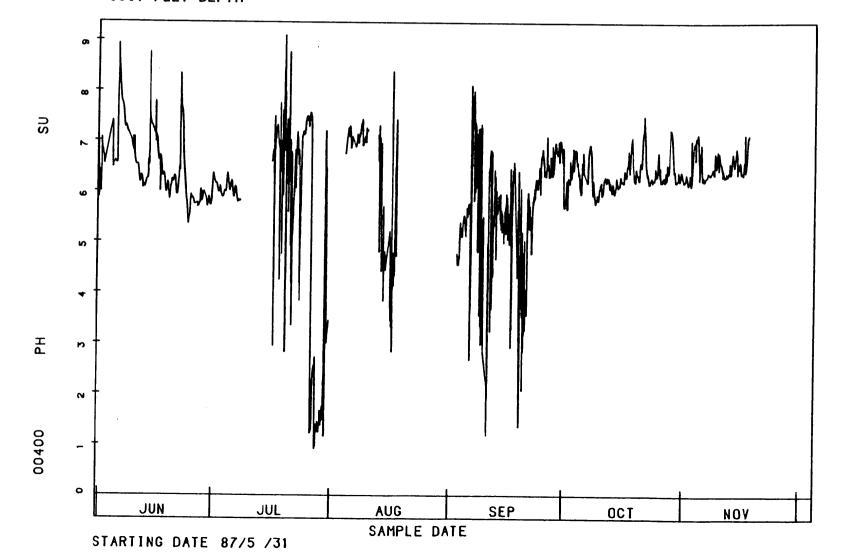


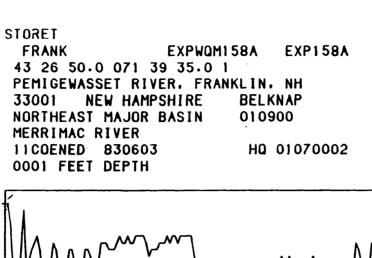
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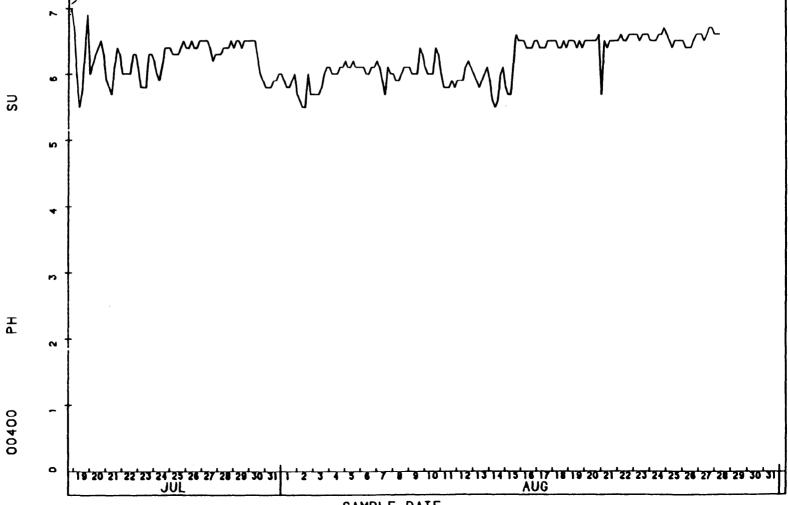


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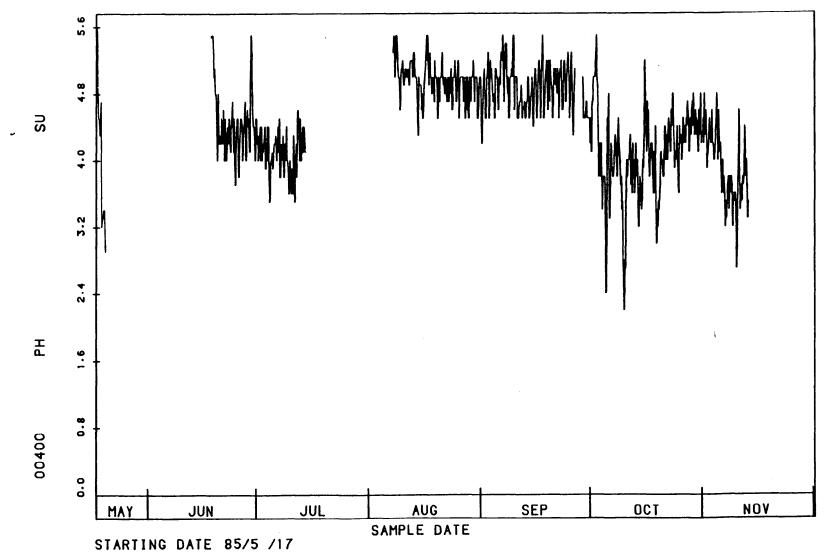
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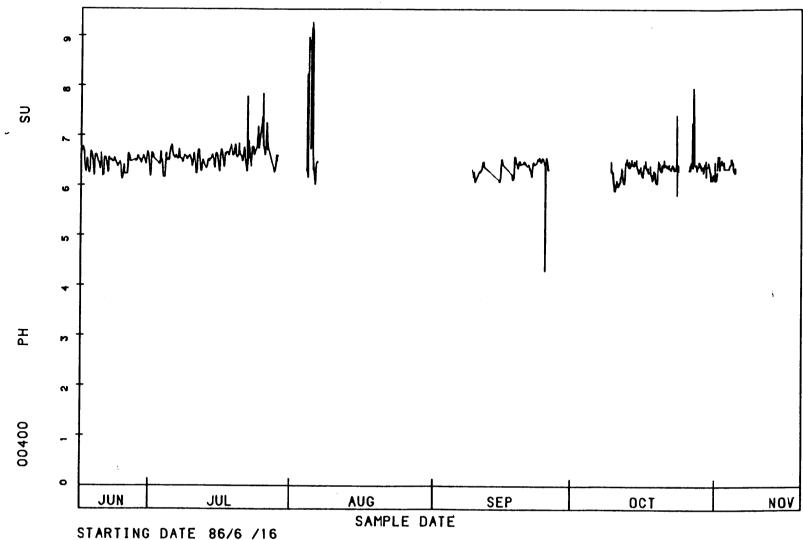




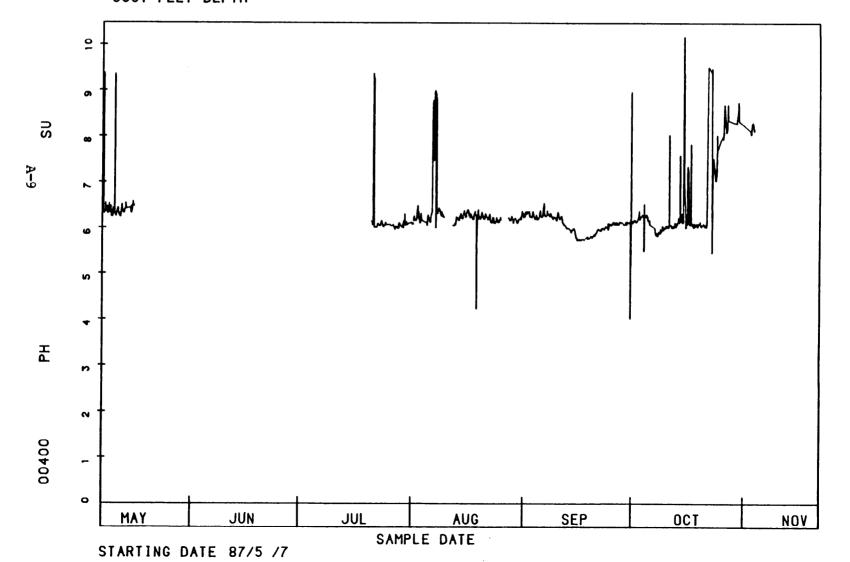


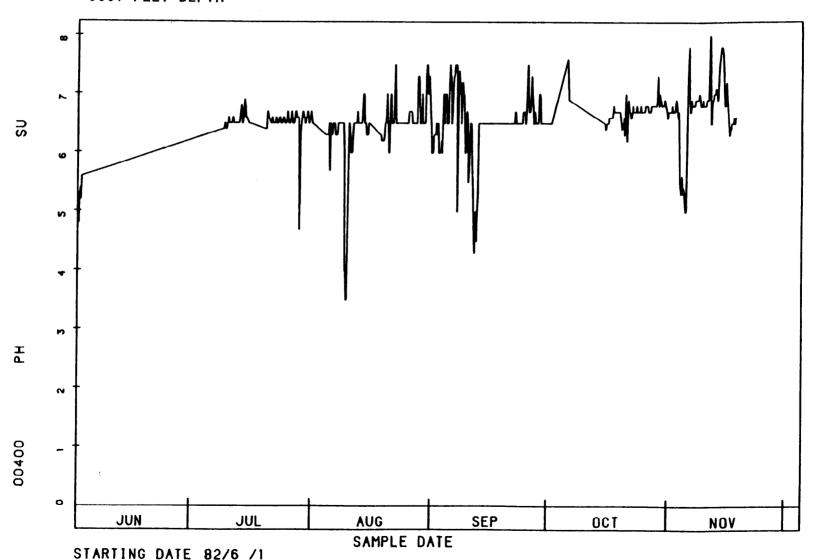
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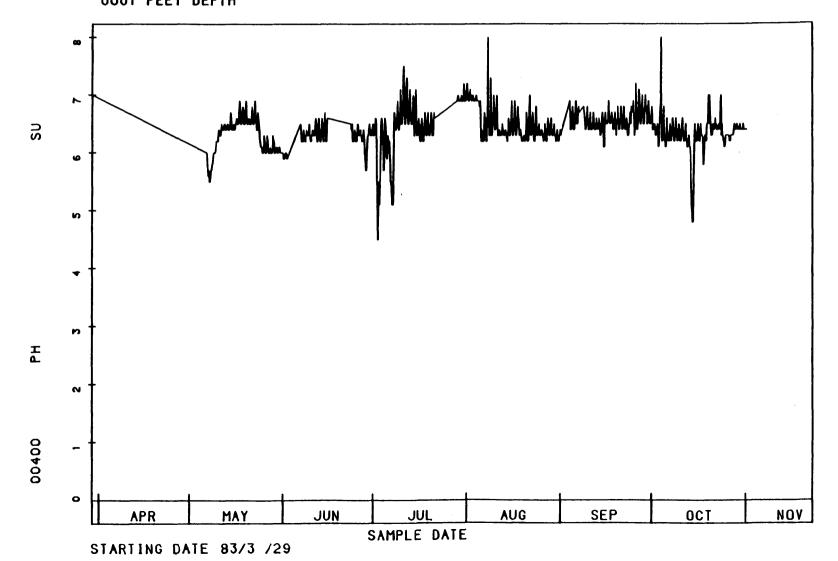




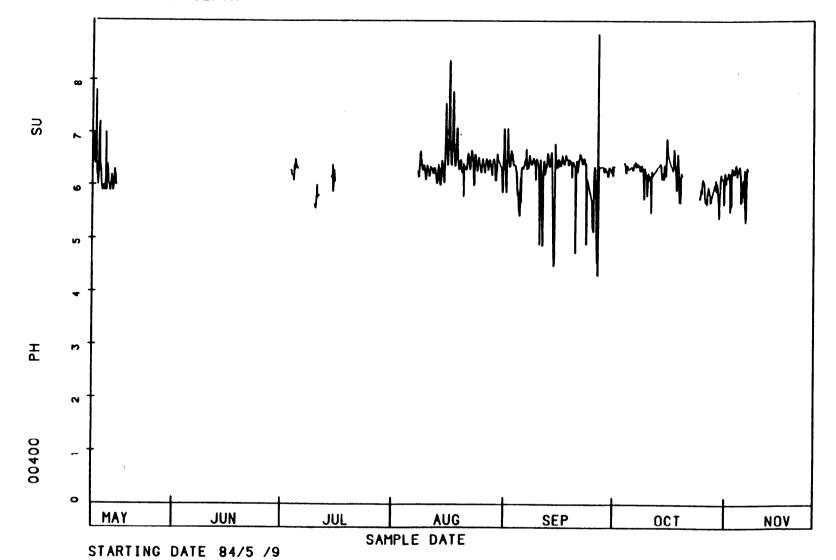
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PEMIGEWASSET RIVER, FRANKLIN, NH
33001 NEW HAMPSHIRE BELKNAP
NORTHEAST MAJOR BASIN 010900
MERRIMAC RIVER
11COENED 830603 HQ 01070002
0001 FEET DEPTH

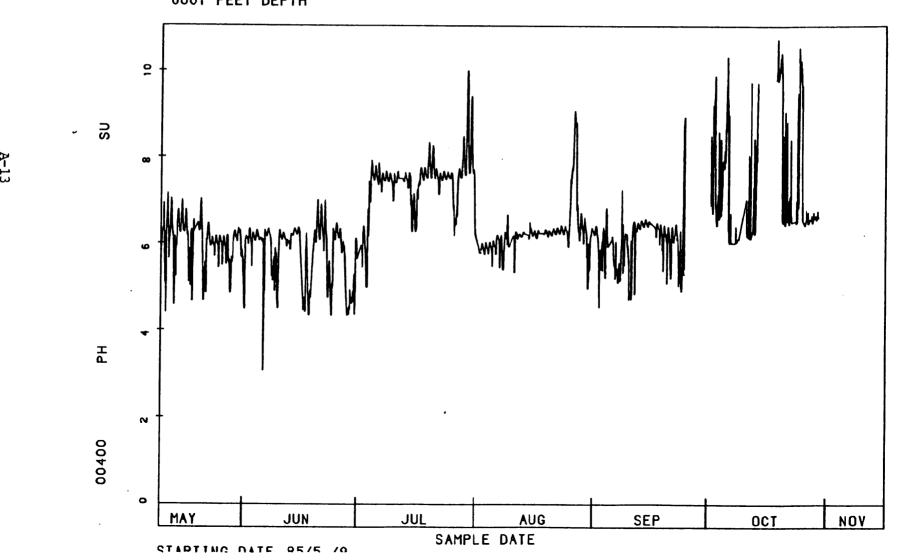




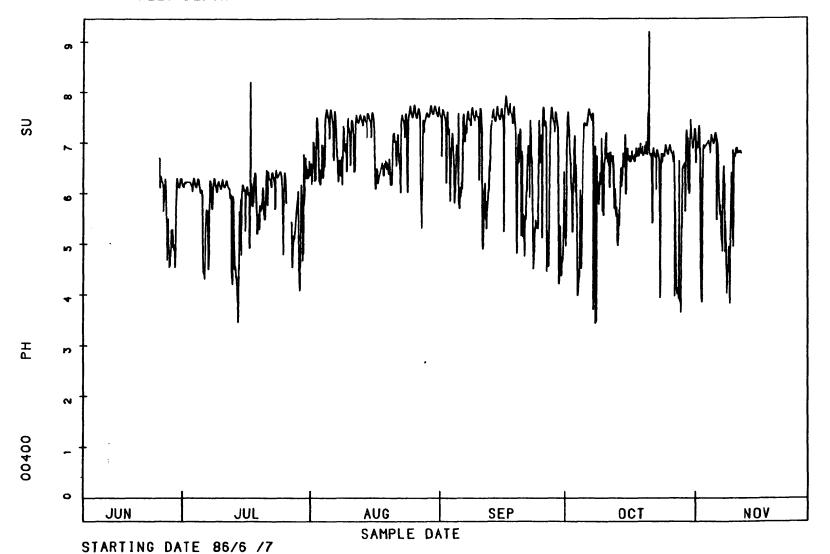


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FRENCH RIVER, OXFORD MA.
25027 MASSACHUSETTS WORCESTER
NORTHEAST 010500
THAMES RIVER
11COENED 810815 HQ 01100001
0001 FEET DEPTH

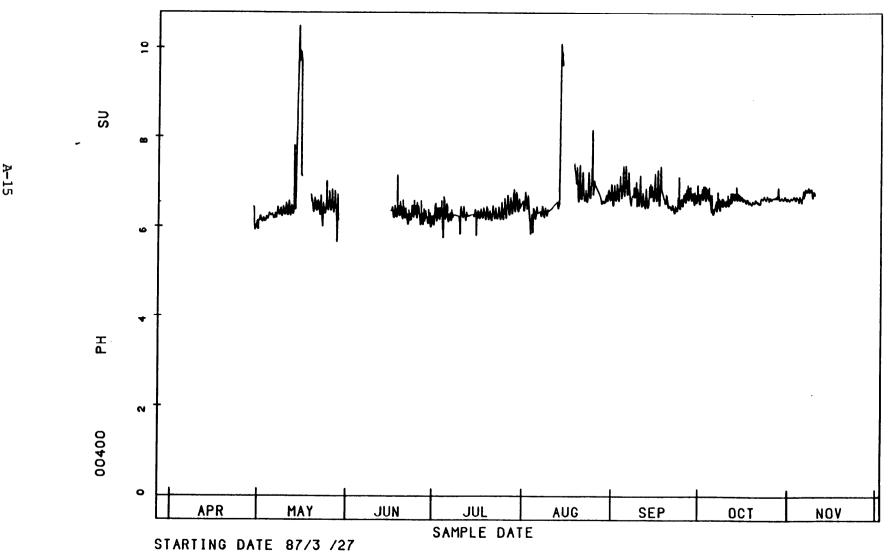




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FRENCH RIVER, OXFORD MA.
25027 MASSACHUSETTS WORCESTER
NORTHEAST 010500
THAMES RIVER
11COENED 810815 HQ 01100001
0001 FEET DEPTH



STORET
HODGV EXPWOM177G EXP177G
42 07 04.0 071 52 52.0 1
FRENCH RIVER, OXFORD MA.
25027 MASSACHUSETIS WORCESTER
NORTHEAST 010500
THAMES RIVER
11COENED 810815 HQ 01100001
0001 FEET DEPTH



STORET

LITT EXPWOM198 EXP198

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MIDDLE BRANCH WESTFIELD R • LITTLEVILLE DAM

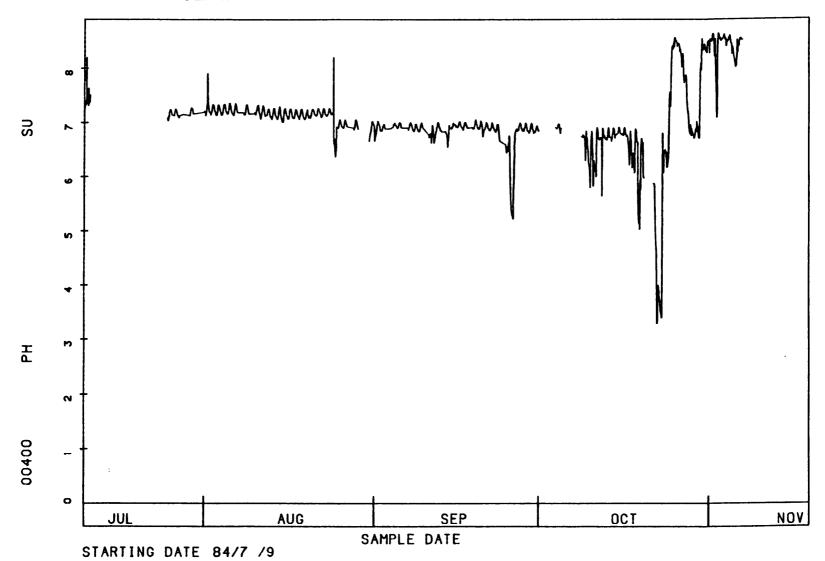
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NORTHEAST 010491

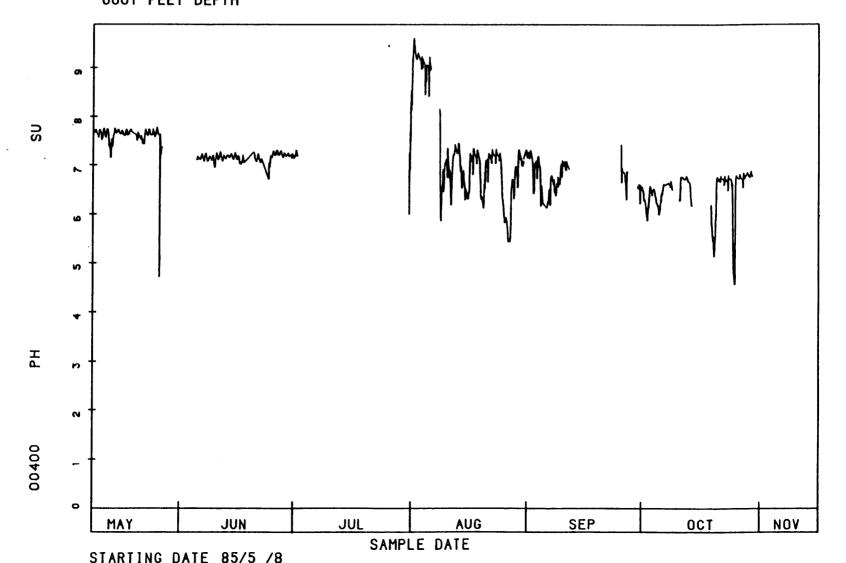
CONNECTICUT RIVER

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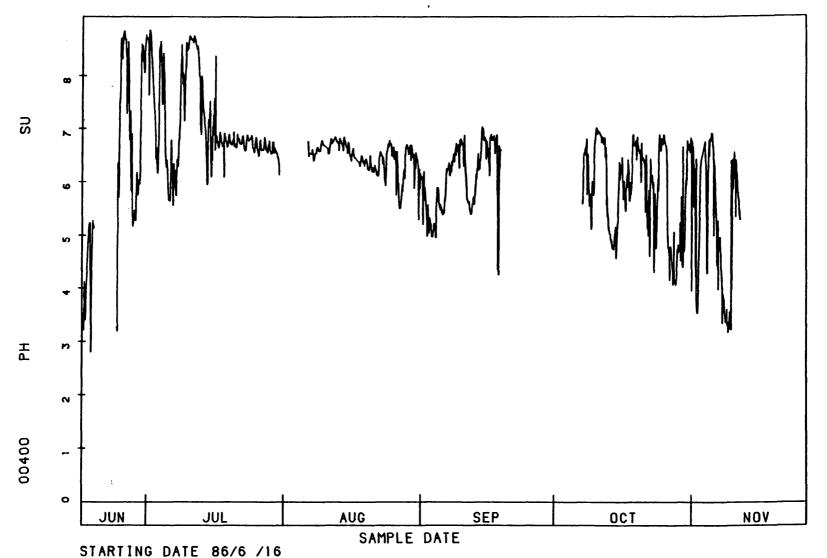
0001 FEET DEPTH



STORET
LITT EXPWOM198 EXP198
42 15 56.0 072 52 50.0 1
MIDDLE BRANCH WESTFIELD R • LITTLEVILLE DAM
25015 MASSACHUSETTS HAMPSHIRE
NORTHEAST 010491
CONNECTICUT RIVER
11COENED 01080206012 0000.940 ON
0001 FEET DEPTH



STORET
LITT EXPWOM198 EXP198
42 15 56.0 072 52 50.0 1
MIDDLE BRANCH WESTFIELD R • LITTLEVILLE DAM
25015 MASSACHUSETTS HAMPSHIRE
NORTHEAST 010491
CONNECTICUT RIVER
11COENED 01080206012 0000.940 ON
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STORET

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MIDDLE BRANCH WESTFIELD R • LITTLEVILLE DAM

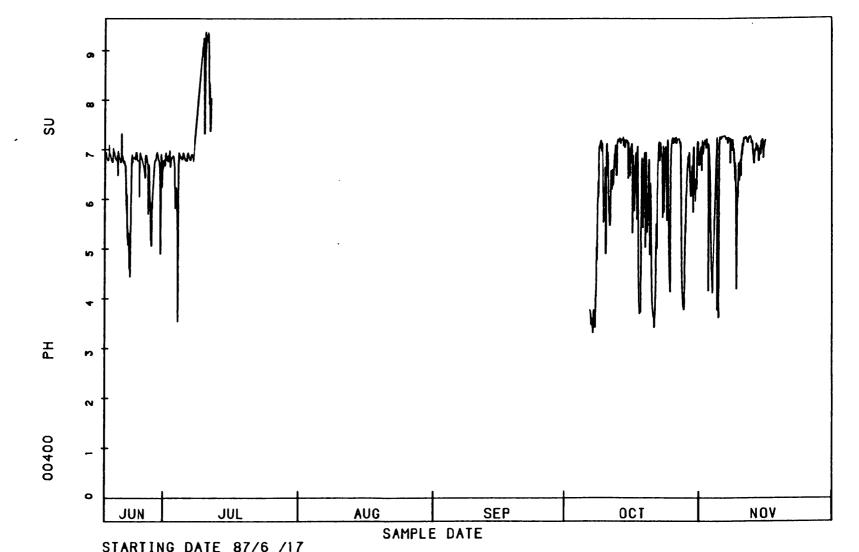
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NORTHEAST 010491

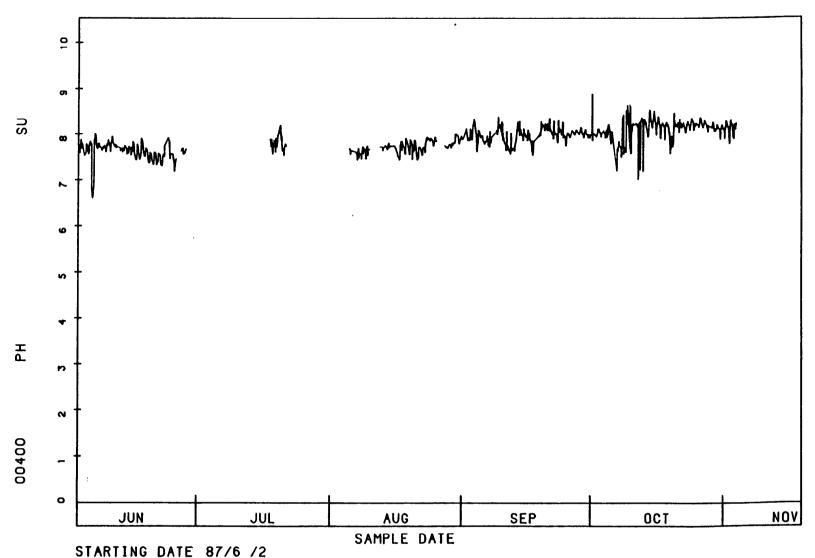
CONNECTICUT RIVER

11 COENED 01080206012 0000.940 ON

0001 FEET DEPTH



STORET
NHART EXPWOM235 EXP235
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OTTAQUECHEE RIVER
50027 VERMONT WINDSOR
NORTHEAST MAJOR BASIN 010434
CONNECTICUT RIVER BASIN
11COENED 870627 01080106
0001 FEET DEPTH



STORET

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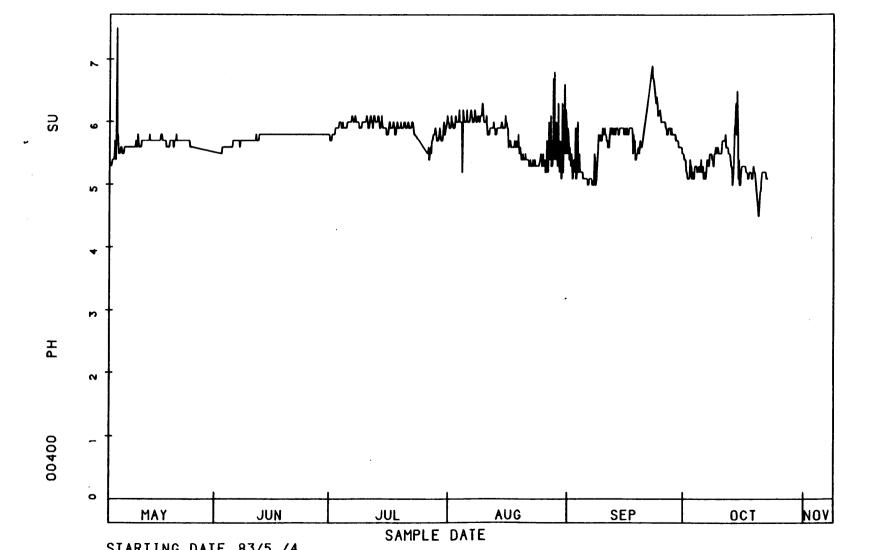
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NORTHEAST 010400

CONNECTICUT RIVER

11COENED 760721 HQ 01080201

0001 FEET DEPTH



STORET

OTTE EXPWOM264 EXP264

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OTTER BROOK BELOW OTTER BROOK DAM

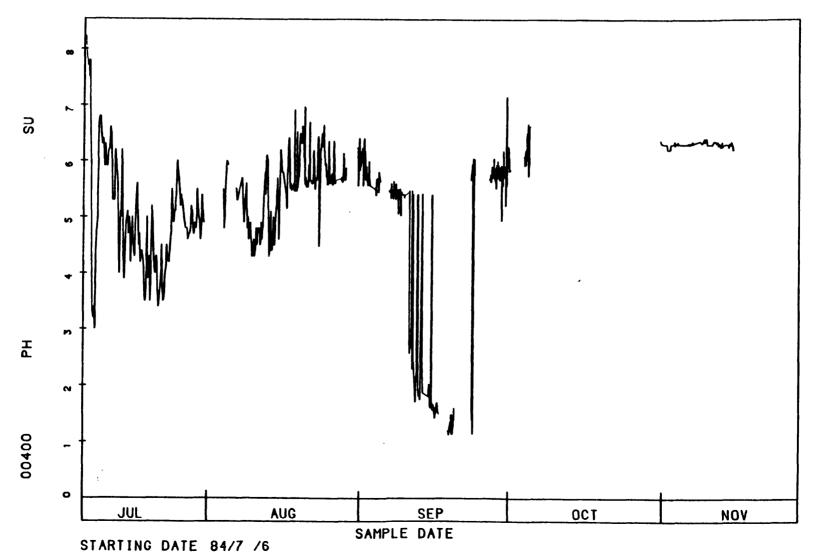
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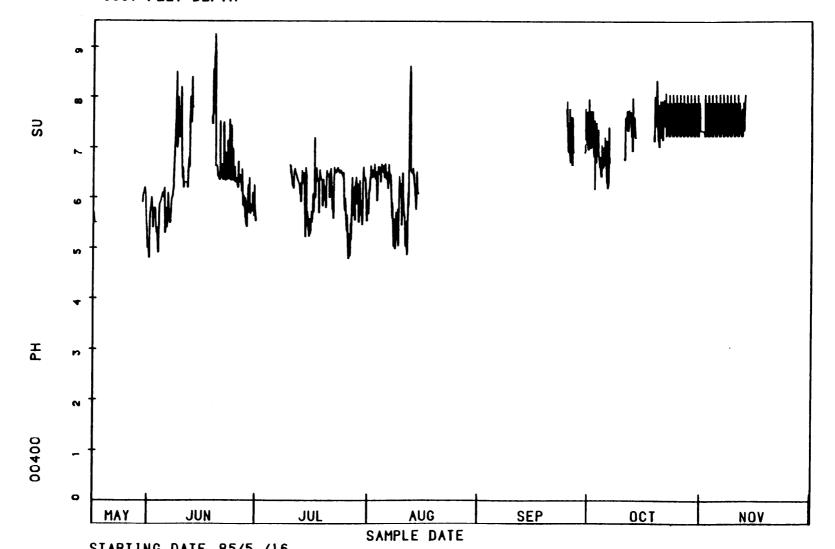
NORTHEAST 010400

CONNECTICUT RIVER

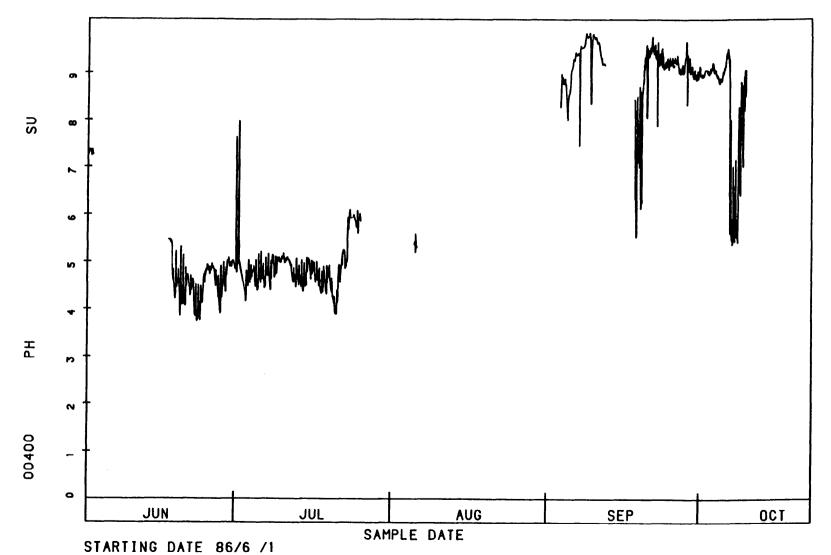
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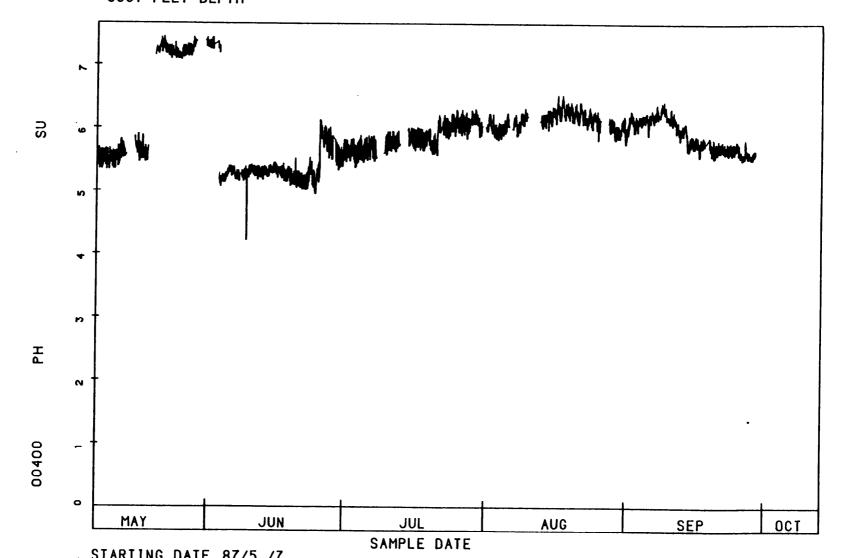
0001 FEET DEPTH



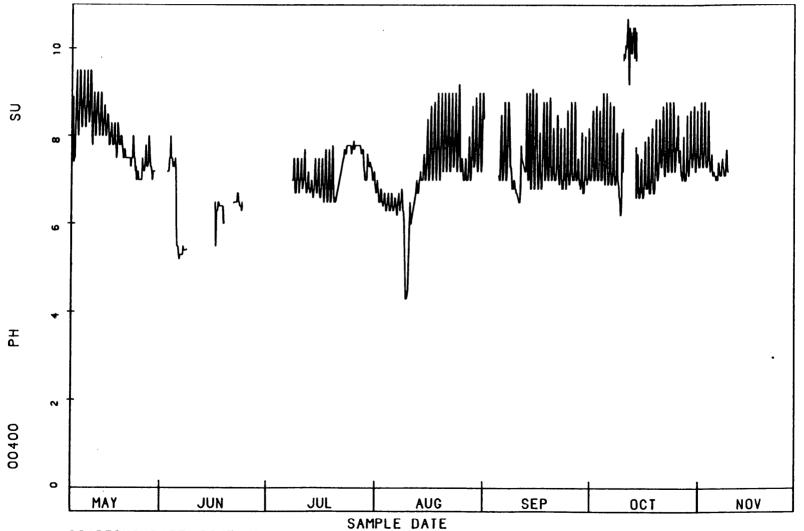


STORET
OTTE EXPWOM264 EXP264
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OTTER BROOK BELOW OTTER BROOK DAM
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NORTHEAST 010400
CONNECTICUT RIVER
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0001 FEET DEPTH



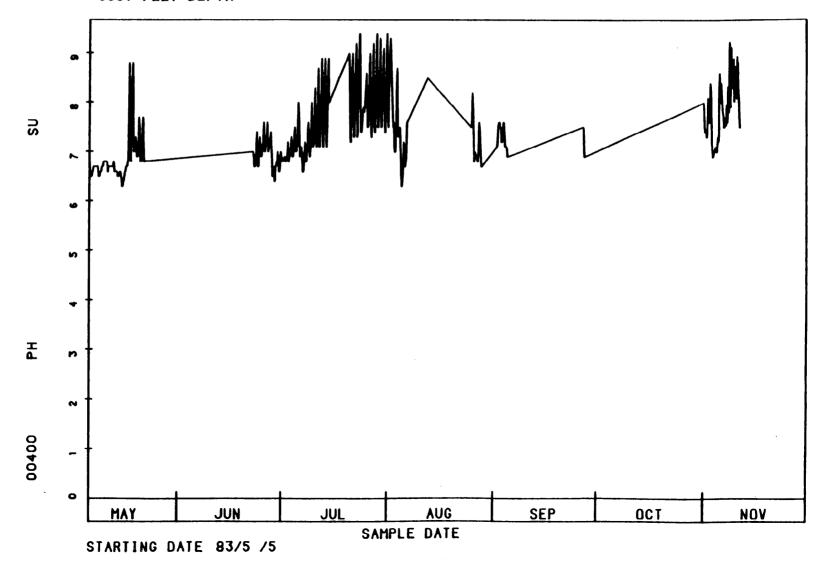


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THOMASTON DAM IMPOUNDMENT, THOMASTON, CT.
09005 CONNECTICUT LITCHFIELD
NORTHEAST 010200
HOUSATONIC RIVER
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0001 FEET DEPTH
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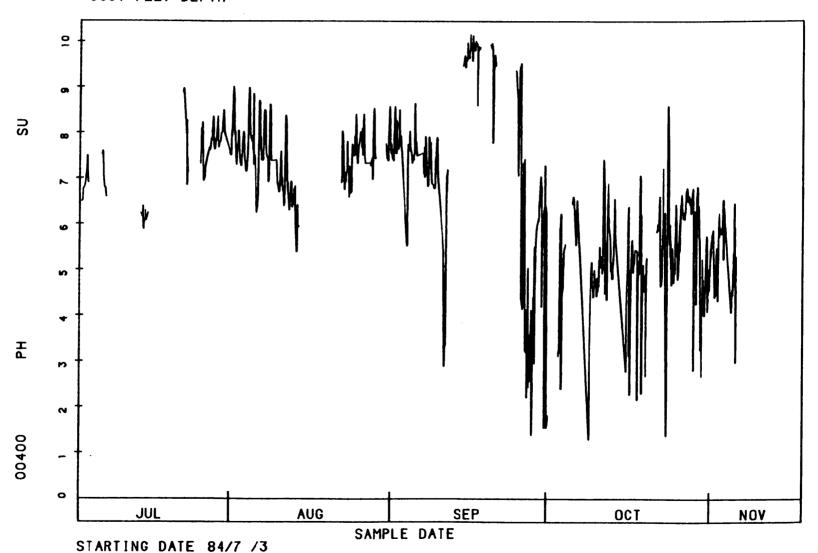


STARTING DATE 82/5 /6

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09005 CONNECTICUT LITCHFIELD
NORTHEAST 010200
HOUSATONIC RIVER
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0001 FEET DEPTH



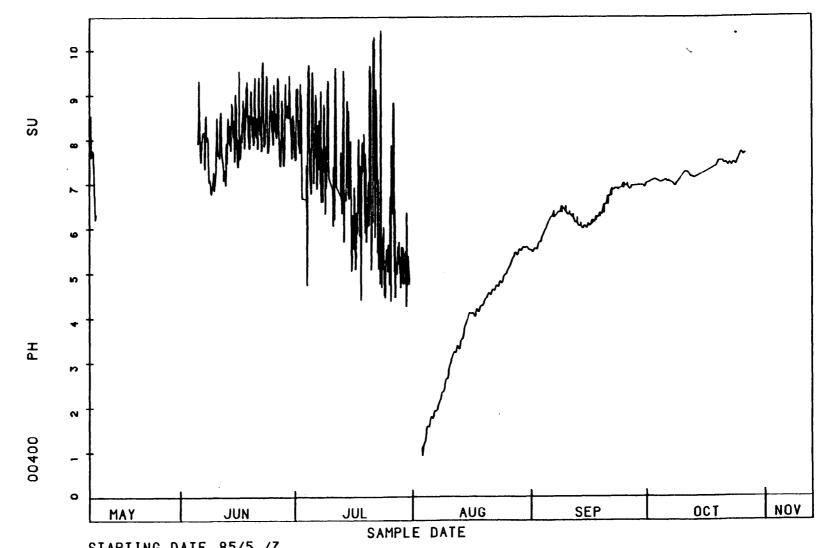
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NORTHEAST 010200
HOUSATONIC RIVER
11COENED 810815 HQ 01100005005 0000.640 OFF
0001 FEET DEPTH



THOM EXPWOM291A EXP291A
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THOMASTON DAM IMPOUNDMENT, THOMASTON, CT.
09005 CONNECTICUT LITCHFIELD
NORTHEAST 010200
HOUSATONIC RIVER

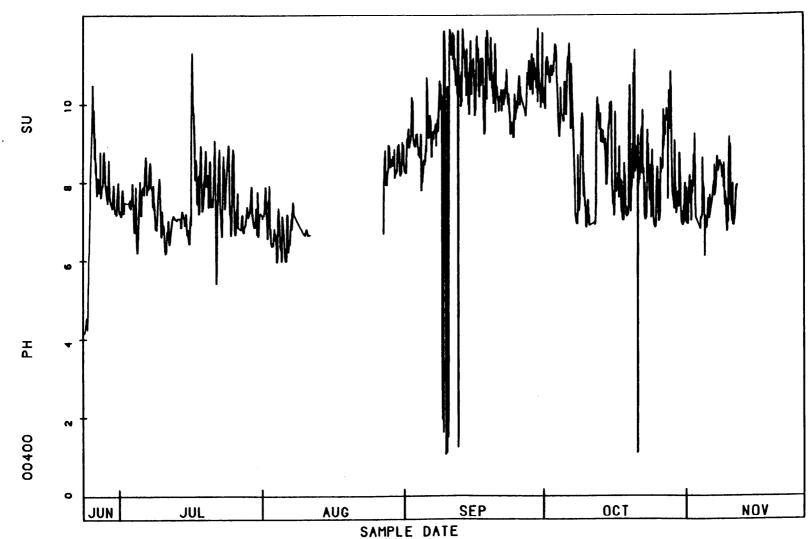
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HQ 01100005005 0000.640 OFF



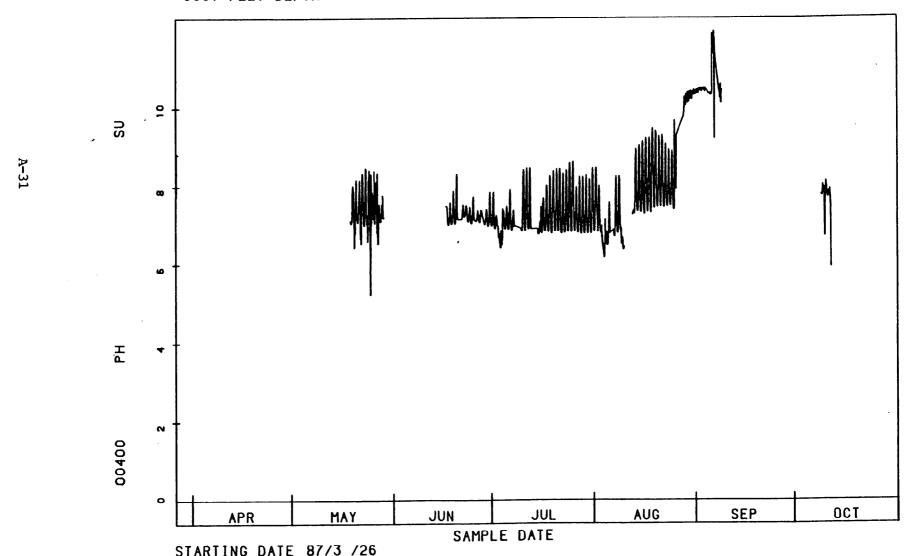
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09005 CONNECTICUT LITCHFIELD
NORTHEAST 010200
HOUSATONIC RIVER
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11COENED 810815 0001 FEET DEPTH HQ 01100005005 0000.640 OFF

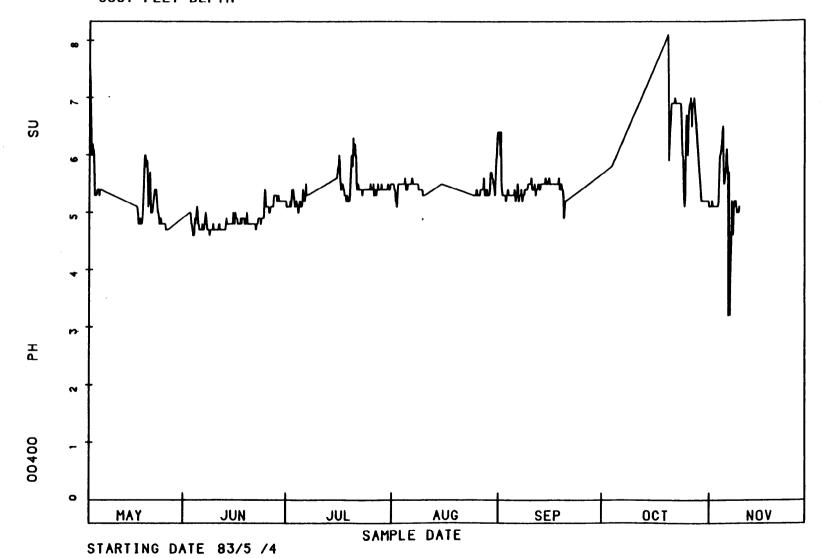


STARTING DATE 86/6 /22

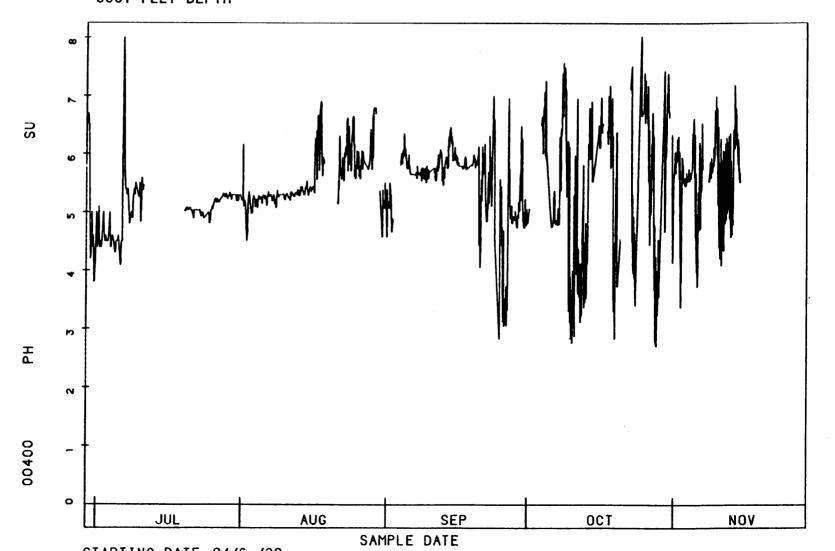
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NORTHEAST 010200
HOUSATONIC RIVER
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0001 FEET DEPTH



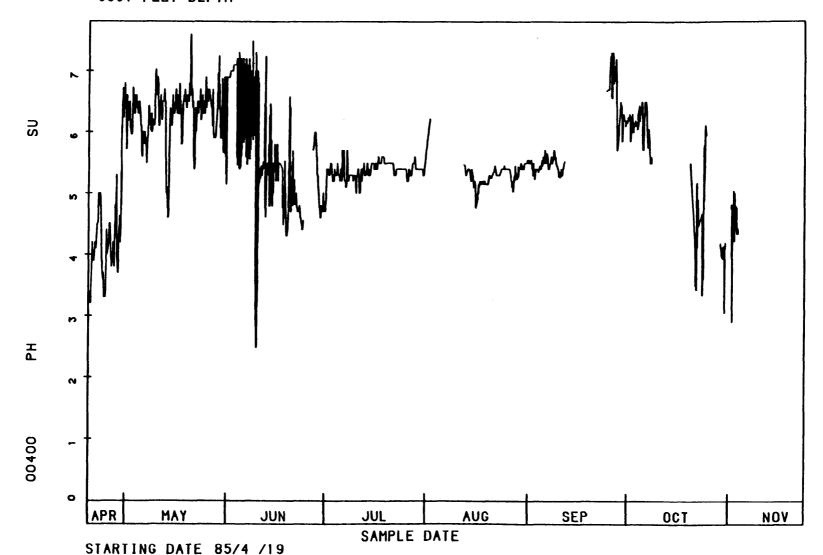
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EAST BRANCH TULLY RIVER, ATHOL
25027 MASSACHUSETTS WORCESTER
NORTHEAST 010400
CONNECTICUT RIVER
11COENED 810815 HQ 01080202
0001 FEET DEPTH



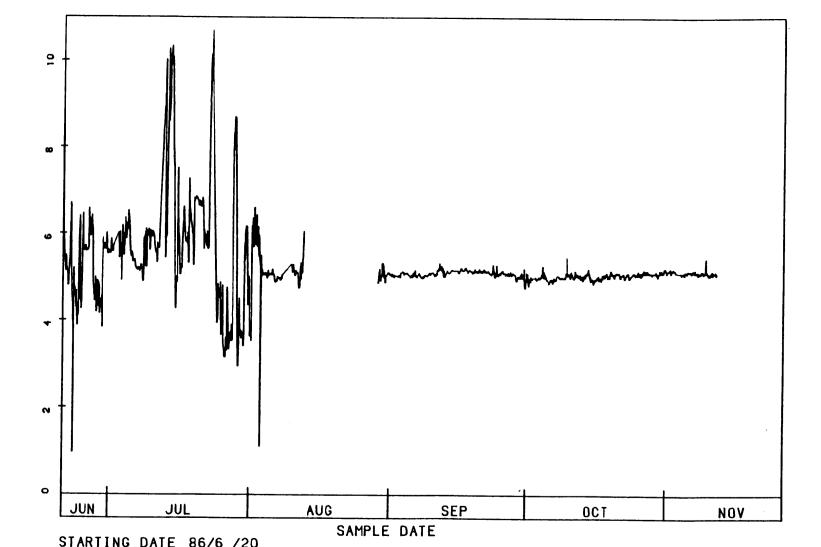
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25027 MASSACHUSETTS WORCESTER
NORTHEAST 010400
CONNECTICUT RIVER
11COENED 810815 HQ 01080202
0001 FEET DEPTH



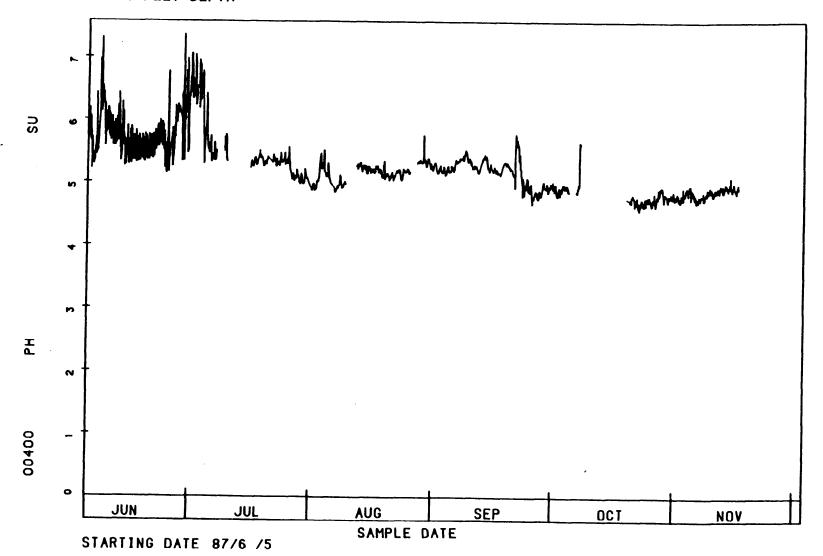
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NORTHEAST 010400
CONNECTICUT RIVER
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0001 FEET DEPTH



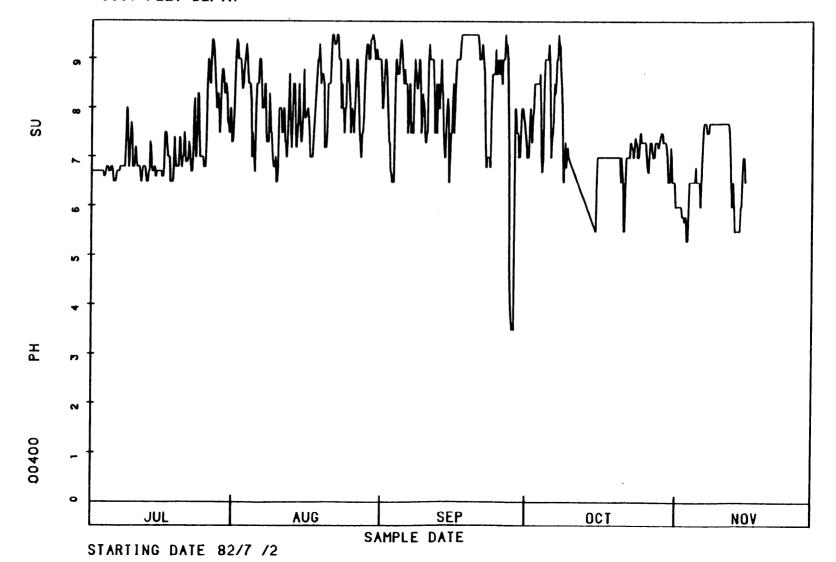
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NORTHEAST 010400
CONNECTICUT RIVER
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0001 FEET DEPTH



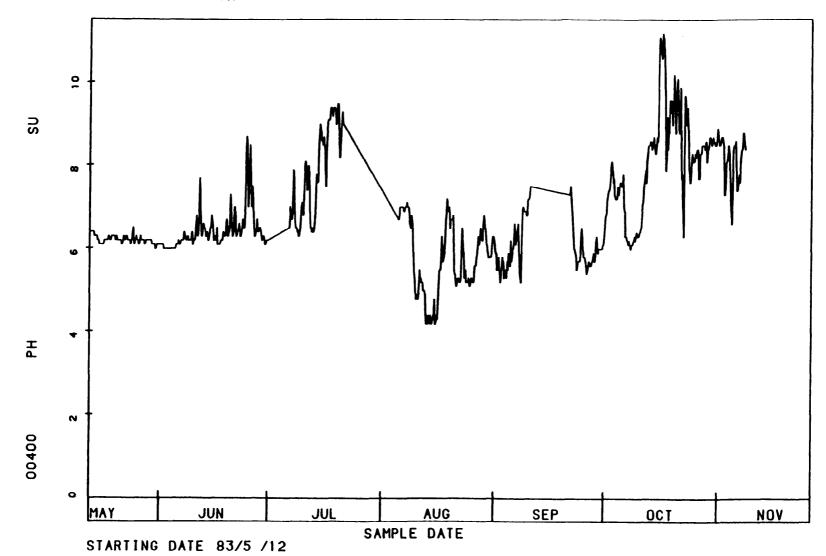
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NORTHEAST 010400
CONNECTICUT RIVER
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0001 FEET DEPTH



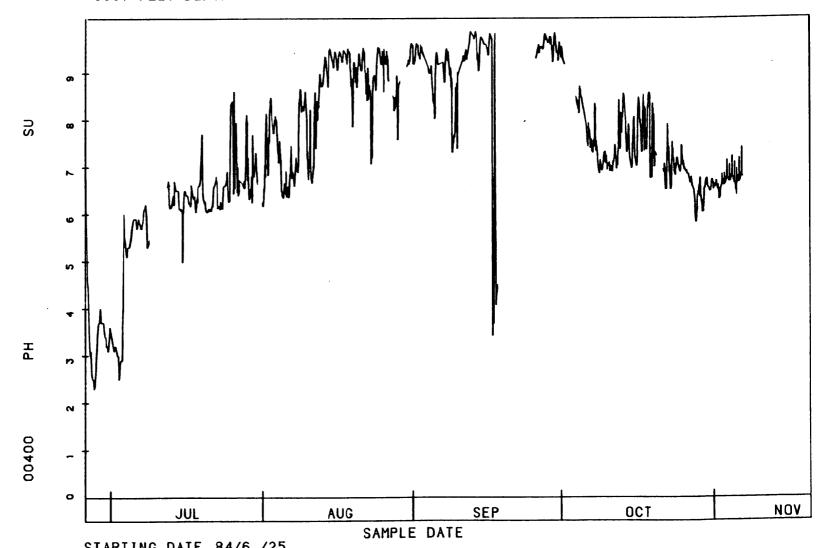
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WTHO EXPWOM347 EXP347
41 56 46.0 071 54 05.0 1
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09015 CONNECTICUT WINDHAM
NORTHEAST 010500
THAMES RIVER
11COENED 760721 01100001005 0002.910 ON
0001 FEET DEPTH



STORET
WTHO EXPWOM347 EXP347
41 56 46.0 071 54 05.0 1
QUINEBAUG RIVER BELOW WEST THOMPSON DAM
09015 CONNECTICUT WINDHAM
NORTHEAST 010500
THAMES RIVER
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0001 FEET DEPTH

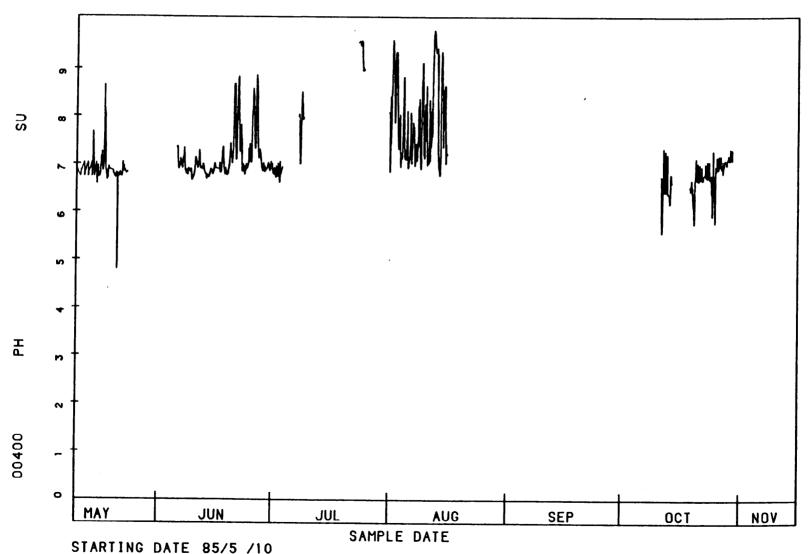


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WTHO EXPWQM347 EXP347
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QUINEBAUG RIVER BELOW WEST THOMPSON DAM
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NORTHEAST 010500
THAMES RIVER
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0001 FEET DEPTH



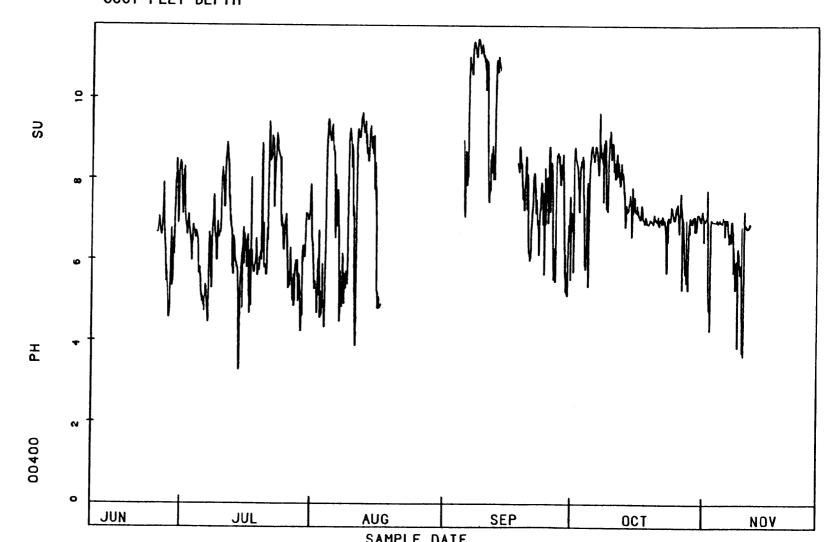


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QUINEBAUG RIVER BELOW WEST THOMPSON DAM
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NORTHEAST 010500
THAMES RIVER
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0001 FEET DEPTH



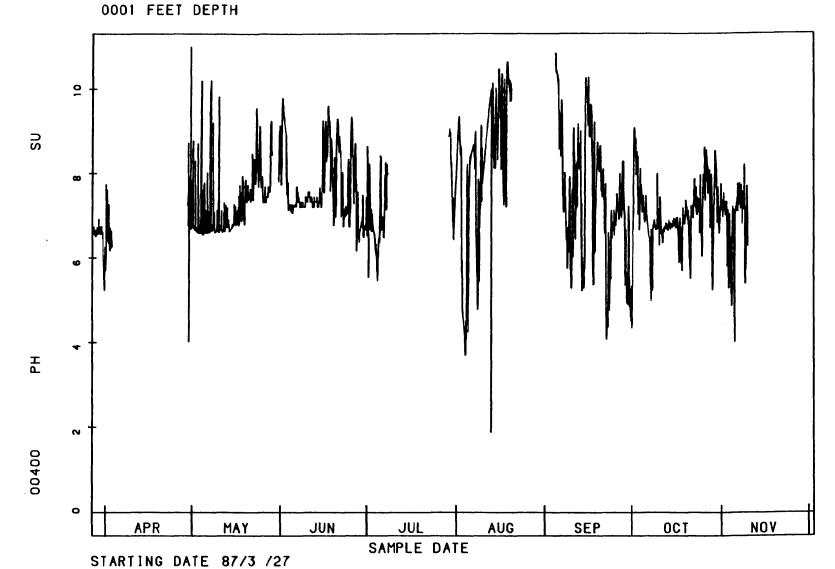


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09015 CONNECTICUT WINDHAM
NORTHEAST 010500
THAMES RIVER
11COENED 760721 01100001005 0002.910 ON
0001 FEET DEPTH



STORET WTHO EXPWQM347 **EXP347** 41 56 46.0 071 54 05.0 1 QUINEBAUG RIVER BELOW WEST THOMPSON DAM 09015 CONNECTICUT WINDHAM NORTHEAST 010500 THAMES RIVER 11COENED 760721

01100001005 0002.910 DN



APPENDIX B

Precipitation Data Collected at NED Projects

ACID RAIN SAMPLES

dGL ₽	PROJECT	STORM DATE	ρH	C1-	NO3-N	J-P	04 504
2785	Buffumville Dam	4/18-4/21/87	5.40	1.9	0.76	0.	36 3.1
2786	Buffumville Dam	4/23/87	4.30	1.1	< 0.05	< 0.	
2787	Buffueville Dam	4/27/87	7.45				
2788	Buffumville Dam	5/2/87	4.30				
2789	Buffumville Dam	5/5-5/6/87	3.75				
2790	Buffumville Dam	5/23/87	3.80				
2791	Buffumville Dam	5/27/87	3.85				
2792	Buffumville Dam	5/29/87	3.80	5.0	0.71	0.4	19 7.3
2799	Buffumville Dam	6/4/87	4.00	2.8	0.99	0.3	
2900	Buffunville Dam	6/8/87	4.20	1.0	1.02	< 0.1	
2801	Buffumville Dam	5/13/87	4.20	1.0	0.56	< 0.2	
2802	Buffumville Dam	5/23/87	3.90	1.4	1.00	< 0.	
2903	Buffumville Dam	6/27/87	4.40	0.8	0.23	(0.2	
2804	Buffumville Dam	6/30/87	4.20	0.9	0.31	< 0.5	
2814	Buffunville Dam	7/3/87	3.80	1.6	0.73	< 0.1	
2915	Suffumville Dam	7/10/87	4.20	2.6	1.06	0.3	
2821	Buffumville Dam	9/3/87	5.70	0.3	0.56	0.9	
2822	Buffunville Dam	8/10/87	3.80	0.5	0.40	< 0.1	
5894	Buffumville Dam	5/11/88	4.40	0.7	0.41	< 0.1	
3895	Buffumville Dam	5/17/89	3.80	0.6	1.74	⟨ 0.1	
3896	Buffumville Dam	5/21/88	4.20	0.6	0.34	⟨ 0.1	
3897	Buffunville Dam	5/24/88	4.10	0.5	0.61	← 0.1	
3898	Buffumville Dam	5/25/88	4.20	0.5	0.20	⟨ 0.1	
3899	Buffueville Dam	6/4/88	3.80	0.9	1.53	(0.1	
4 250	Buffunville Dam	6/17/88	3.50	2.1	2.20	₹ 0.1	.0 2.2
5083	Buffusville Das	7/20/88	3.30				
5084.	Buffumville Dam	7/24/88	4.00				
5085	Buffumville Dam	8/1/88	3.50				
5096	Buffumville Dam	8/25/88	3.90				
5087	Buffumville Dam	8/30/98	4.40				
5088	Buffueville Dam	9/4/88	4.20				

ACID RAIN SAMPLES

₩3L #	PROJECT	STORM DATE	pН	C1-	NO3-N	0	-P04	SO4
2796	Thomaston Dam	not recorded	4.35					
27 9 7	Thomaston Dam	5/27-5/28/87	7.40	3.2	0.30		7.40	22.2
2810	Thomaston Dam	6/1-6/5/87	5.00	0.6	0.75		0.51	5.7
2811	Thomaston Dam	not recorded	4.50	0.7	1.16		0.65	10.3
2812	Thomaston Dam	6/26-6/29/87	4.30	0.7	0.50		0.25	4.8
2820	Thomaston Dam	not recorded	7.00	8.6	0.59		1.98	9.3
2830	Thomaston Dam	not recorded	4.40	1.1	0.92		0.19	8.3
2831	Thomaston Dam	not recorded	3.70	0.6	0.79	<	0.10	9.2
2835	Thomaston Dam	not recorded	3.90	0.5	0.60	(0.10	4.1
2836	Thomaston Dam	not recorded	4,40	1.1	0.22	<	0.10	2.3
2837	Thomaston Dam	not recorded	3.80	5.0	0.82	<	0.10	4.5
2938	Thomaston Dam	not recorded	4.50	0.7	0.17	<	0.10	1.7
3888	Thomaston Dam	nat recorded	3.80	1.2	0.85	<	0.10	5.6
3889	Thomaston Dam	not recorded	3.80	0.8	0.67	<	0.10	5.3
4126	Thomaston Dam	not recorded	4.10	0 .9	0.52	〈	0.10	3.8
4392	Thomaston Dam	not recorded	4.00	0.7	0.53	(0.10	3.9
4393	Thomaston Dam	not recorded	5.90	2.0	1.97		2.59	14.3
4394	Thomaston Dam	not recorded	4.10	0.8	0.99	₹	0.10	8.7
4395	Thomaston Dam	not recorded	4.20	0.6	0.34	<	0.10	2.5
4681	Thomaston Dam	not recorded	3.60	0.8	1.56		0.1	8.9

ACID RAIN SAMPLES

#QL #	PROJECT	STORM DATE	ρН	C1-	N03-N	o-P04	S 04
2793	North Hartland Lake	5/23/87	4.25				
2794	North Hartland Lake	5/26/87	5.00	1.0	0.22	< 0.10	2.8
2795	North Hartland Lake	5/29/87	4.20	18.8	⟨ 0.05	₹ 0.10	15.9
2805	North Hartland Lake	6/4-6/5/87	4.20	0.6	0.39	₹ 0.10	3.5
2906	North Hartland Lake	5/9/97	4.20	0.9	0.67	₹ 0.10	5.2
2807	North Hartland Lake	6/15/87	4.20	0.9	0.43	€ 0.10	6.1
2908	North Hartland Lake	6/23/87	4.00	0.8	0.24	€ 0.10	2.5
2909	North Hartland Lake	6/27/87	5.20	0.7	0.11	← 0.10	1.5
2816	North Hartland Lake	7/2/87	4.60	0.9	0.17	0.10	2.3
2817	North Hartland Lake	7/4/87	4.00	2.3	0.79	0.10	8.2
2819	North Hartland Lake	7/14/87	4.40	0 .9	0.25	0.10	2.8
2819	North Hartland Lake	7/24/87	3.90	1.6	0.70	0.11	9.1
2823	North Hartland Lake	8/9-8/10/87	4.40	1.0	0.18	(0.10	2.9
2824	North Hartland Lake	8/10/87	3.80	1.7	0.52	0.12	5.6
2825	North Hartland Lake	8/19/87	6.00	2.4	0.50	0.28	3.4
2826	North Hartland Lake	8/22/87	4.20	1.1	0.34	(0.10	3.3
2927	North Hartland Lake	8/25-8/26/87	6.20	0.7	0.24	0.14	2.6
2828	North Hartland Lake	8/28-8/29/87	4.20	0.5	0.30	⟨ 0.10	2.8
2829	North Hartland Lake	8/29/87	4.50	0.8	0.13	€ 0.10	1.7
2932	North Hartland Lake	9/8/87	7.20	0.5	0.11	1.11	2.3
2833	North Hartland Lake	9/13/87	5.10	0.9	0.14	⟨ 0.10	2.2
2934	North Hartland Lake	9/18/9/21/87	5.30	0.5	0.18	₹ 0.10	1.8
2917	North Hartland Lake	10/3-10/4/87	5.00	0.6	0.15	€ 0.10	1.5
2915	North Hartland Lake	10/11/87	4.60	0.9	0.35	₹ 0.10	2.7
2916	North Hartland Lake	10/11/87	2.80	1.1	0.17	₹ 0.10	11.2
2918	North Hartland Lake	10/20-10/21/87	3.20	9.6	1.88	0.10	7.9
2919	North Hartland Lake	10/21/87	3.40	0.5	0.88	0.10	3.9
2920	North Hartland Lake	10/28/87	4.00	0.6	0.13	⟨ 0.10	1.9
3890	North Hartland Lake	4/29-5/1/88	4.00	0.5	0.41	0.10	2.4
3891	North Hartland Lake	5/12/98	3.80	0.6	0.87	0.10	5.4
3892	North Hartland Lake	5/17/88	3.70	0.6	1.04	€ 0.10	7.8
3893	North Hartland Lake	5/20/88	3.90	0.6	0.50	₹ 0.10	3.8
3906	North Hartland Lake	5/26/88	4.40	0.5	0.20	(0.10	2.3
3907	North Hartland Lake	5/31/88	4.00	0.6	0.93	⟨ 0.10	5.6
4179	North Hartland Lake	not record ed	5.00	0.9	0.29	₹ 0.10	3.3
4180	North Hartland Lake	7/2-7/3/88	4.80	3.3	0.30	0.27	2.2
4181	North Hartland Lake	6/28/88	4.20	4.6	0.75	0.40	0.8
4321	North Hartland Lake	7/14/88	3.80	4.0	0.37	0.30	6. 4
4322	North Hartland Lake	7/17/88	4.00	0.8	0.39	⟨ 0.10	5.2
4536	North Hartland Lake	7/19/88	4.10	3.2	0.84	0.24	5.3
4537	North Hartland Lake	7/21-7/22/88	4.90	0.6	0.16	< 0.10	2.0
4538	North Hartland Lake	7/24/88	4.60	3.3	0.20	0.22	2.1
4539	North Hartland Lake	7/28/88	4.40	2.8	0.38	0.21	3 .5
4540	North Hartland Lake	7/31/88	3.60	1.0	1.81	0.10	12.0
4785	North Hartland Lake	nat recorded	4.00	1.0	0.65	0.10	4.7
4786	North Hartland Lake	not recorded	4.40	1.2	0.29	0.12	3.4
4846	North Hartland Lake	8/23/88	4.70	0.9	0.27	0.10	2.6
4847	North Hartland Lake	8/27-8/29/99	4.60	0.8	0.25	⟨ 0.10	3.2
107/	HOLEH HELLTEHU CEKE	GILI GILIII	7.00	V.0	V. 4J	/ 4.10	2.2

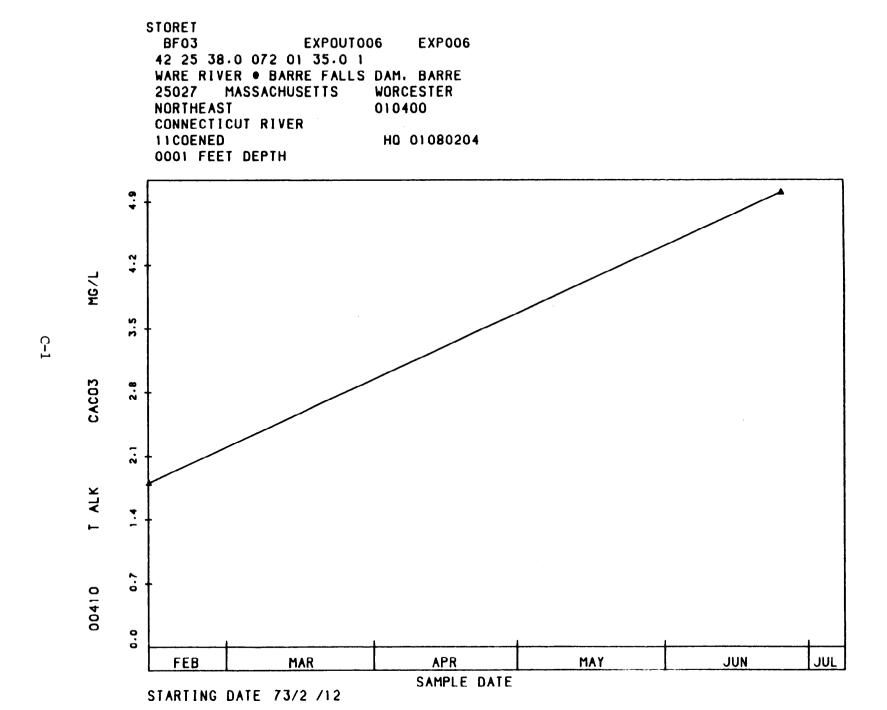
ACID RAIN SAMPLES

#QL #	FROJECT	STORM DATE		рН	C1-	NO3-N		o-P04	S04
2813	Barre Falls Dam	not recorded	4.	45					
4125	Barre Falls Dam	5/25/88	4.	20	1.1	0.99	(0.10	5.4
4396	Barre Falls Dam	7/23/88	4.	00	0.6	0.39	(0.10	2.9
4421	Barre Falls Dam	7/28/88	3.	80	2.1	0.86		0.22	4.4
4535	Barre Falls Dam	7/30/88	3.	30	2.2	0.32	(0.10	49.0
4799	Barre Falls Dam	8/29/88	4.	80	1.4	0.30	₹	0.10	3.0
4816	Barre Falls Dam	8/29-8/30/88	5.	60	1.9	0.26		0.12	2.7
5056	Barre Falls Dam	9/18/88	x 5.	70	- • •				•••

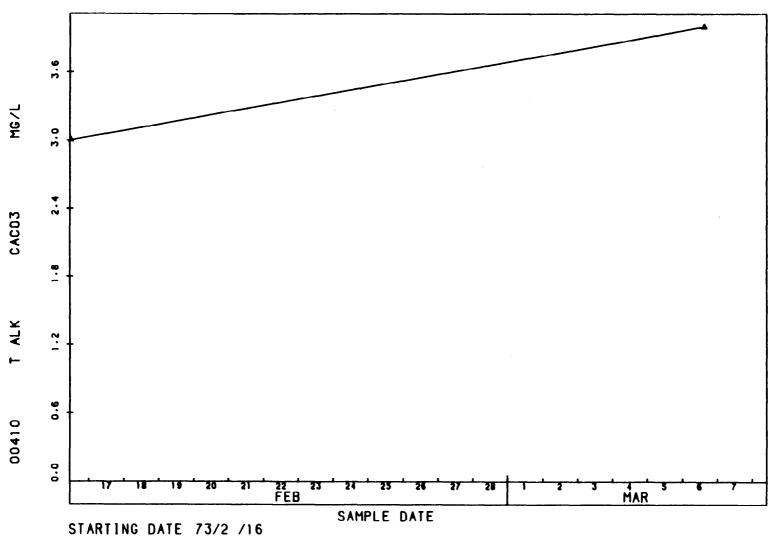
[#] Material floating in sample - including insects.

APPENDIX C

Alkalinity Plots

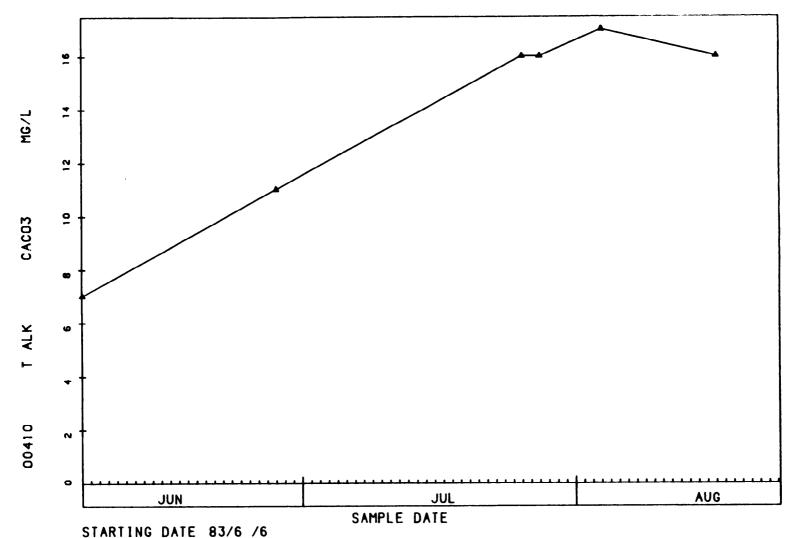


STORET
BH06 EXPOUTO15 EXPO15
42 37 41.0 072 08 39.0 1
MILLERS RIVER. RIE 68. SOUTH ROYALSTON
25027 MASSACHUSETTS WORCESTER
NORTHEAST 010400
CONNECTICUT RIVER
11 COENED HQ 01080202009 0007.900 OFF
0001 FEET DEPTH



STORET FF03 EXPOUT159 EXP159 43 26 50.0 071 39 35.0 1 PEMIGEWASSET RIVER BELOW FRANKLIN FALLS DAM 33001 NEW HAMPSHIRE BELKNAP 010991 NORTHEAST MERRIMACK RIVER 01070002 11 COENED 0001 FEET DEPTH 11978 11979 11982 11983 11975 11980 11981 11972 |1973 11974 11976 11977 MG/L C-3 CAC03 n T ALK 00410 0 SAMPLE DATE

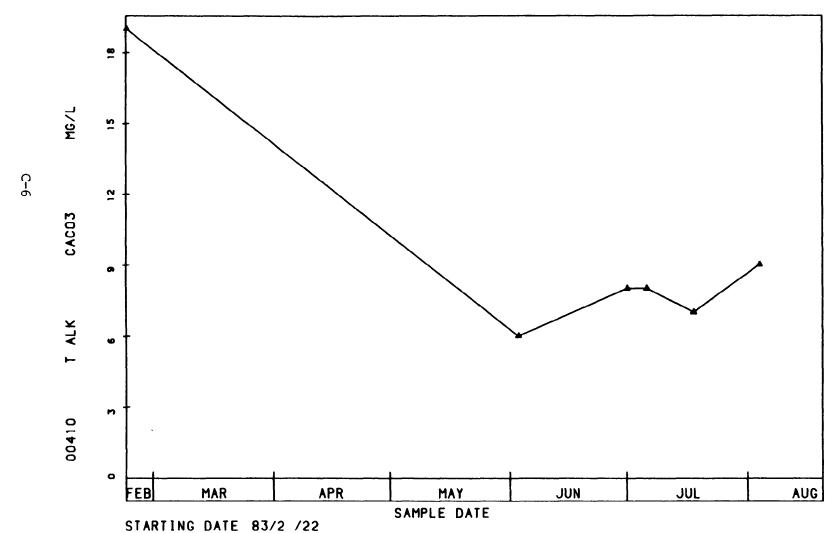
STARTING DATE 71/7 /28

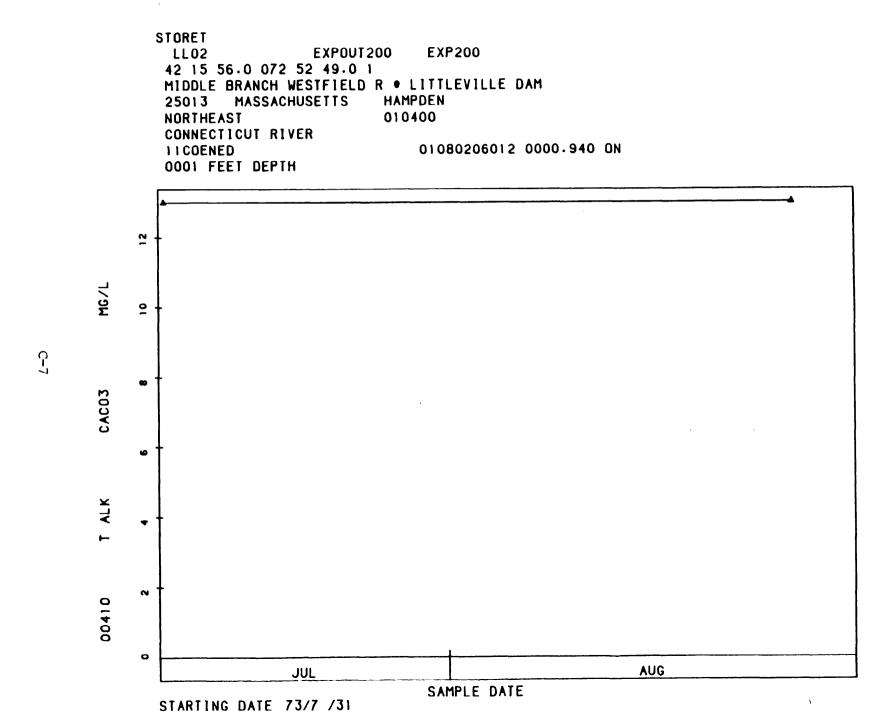


STORET

STARTING DATE 71/8 /2

STORET
LITT EXPWOM198 EXP198
42 15 56.0 072 52 50.0 1
MIDDLE BRANCH WESTFIELD R • LITTLEVILLE DAM
25015 MASSACHUSETTS HAMPSHIRE
NORTHEAST 010491
CONNECTICUT RIVER
11COENED 01080206012 0000.940 ON
0001 FEET DEPTH





STORET

OBO4 EXPOUT258 EXP258

42 56 36.0 072 14 30.0 1

OTTER BROOK BELOW OTTER BROOK DAM

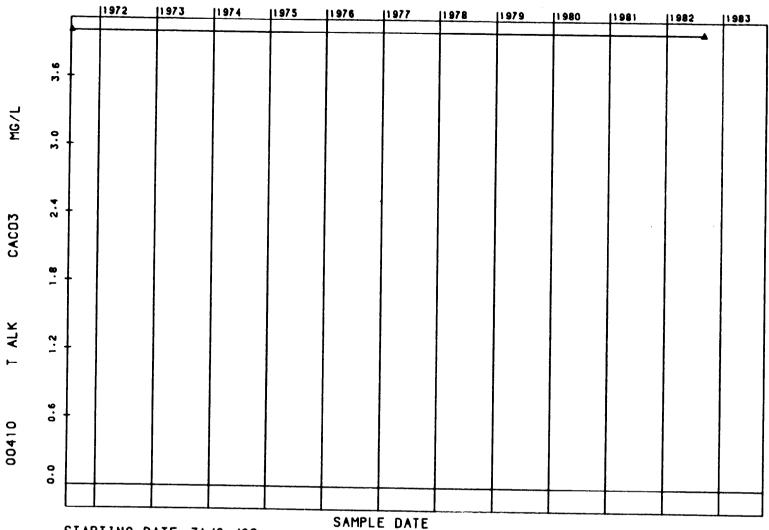
33005 NEW HAMPSHIRE CHESHIRE

NORTHEAST 010400

CONNECTICUT RIVER

11 COENED 01080201

0001 FEET DEPTH



STARTING DATE 71/6 /28

STORET

OTTE EXPWOM264 EXP264

42 56 36.0 072 14 30.0 1

OTTER BROOK BELOW OTTER BROOK DAM

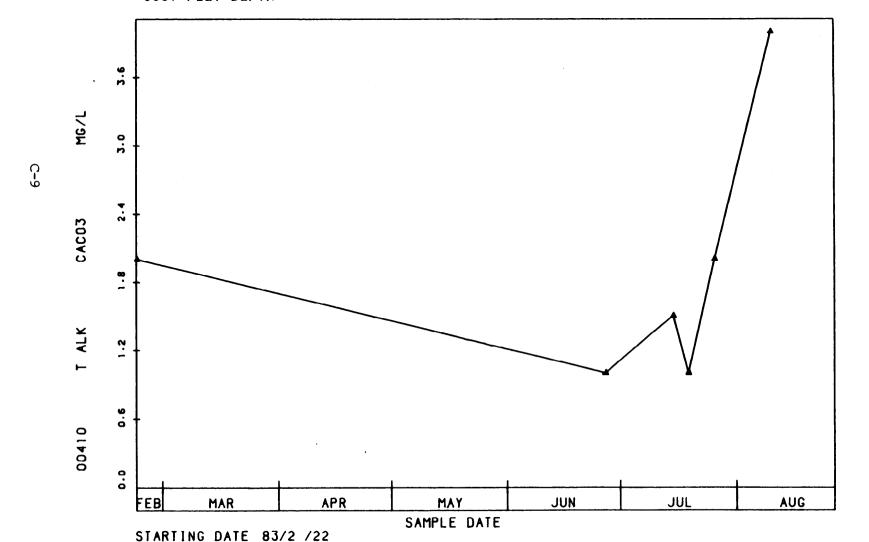
33005 NEW HAMPSHIRE CHESHIRE

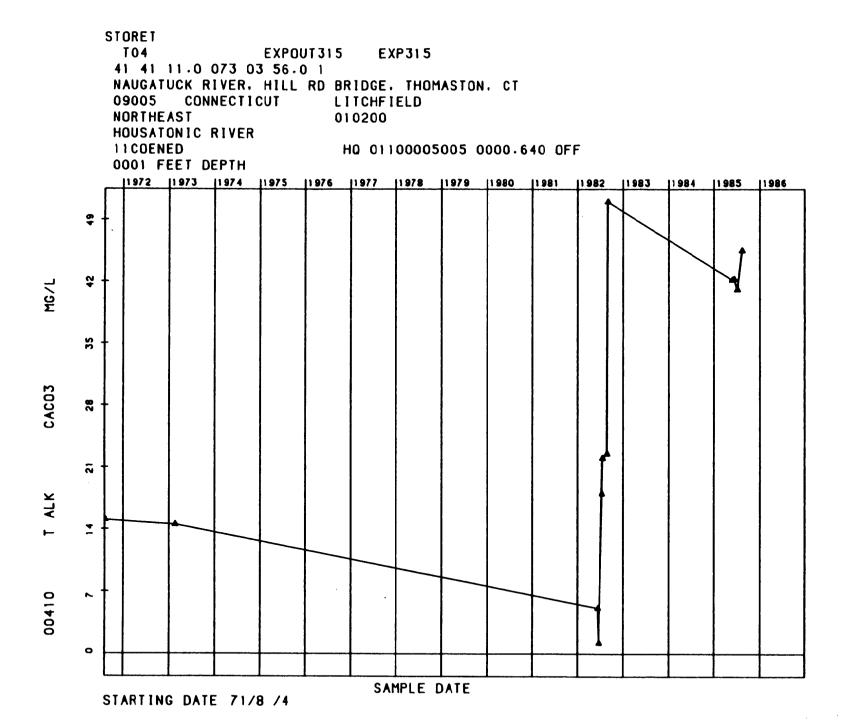
NORTHEAST 010400

CONNECTICUT RIVER

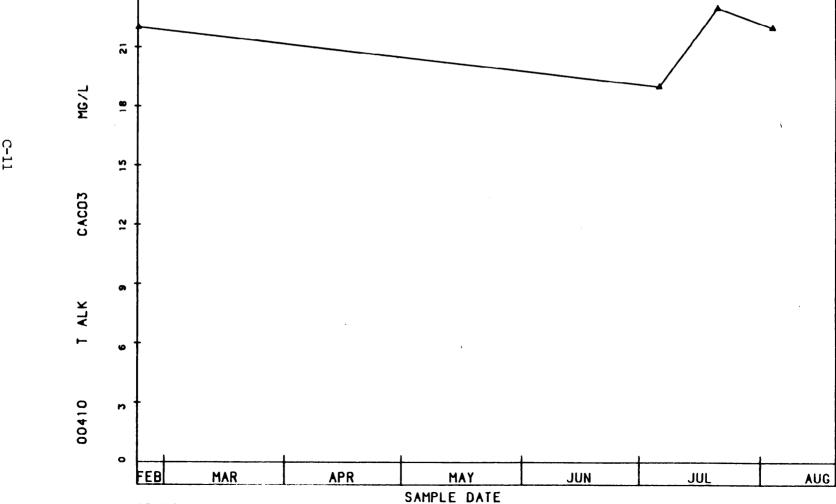
11COENED 760721 HQ 01080201

0001 FEET DEPTH





STORET
THOM EXPWOM291A EXP291A
41 41 11.0 073 03 55.6 1
THOMASTON DAM IMPOUNDMENT. THOMASTON. CT.
09005 CONNECTICUT LITCHFIELD
NORTHEAST 010200
HOUSATONIC RIVER
11COENED 810815 HQ 01100005005 0000.640 OFF
0001 FEET DEPTH



STARTING DATE 83/2 /22

SAMPLE DATE

STORET

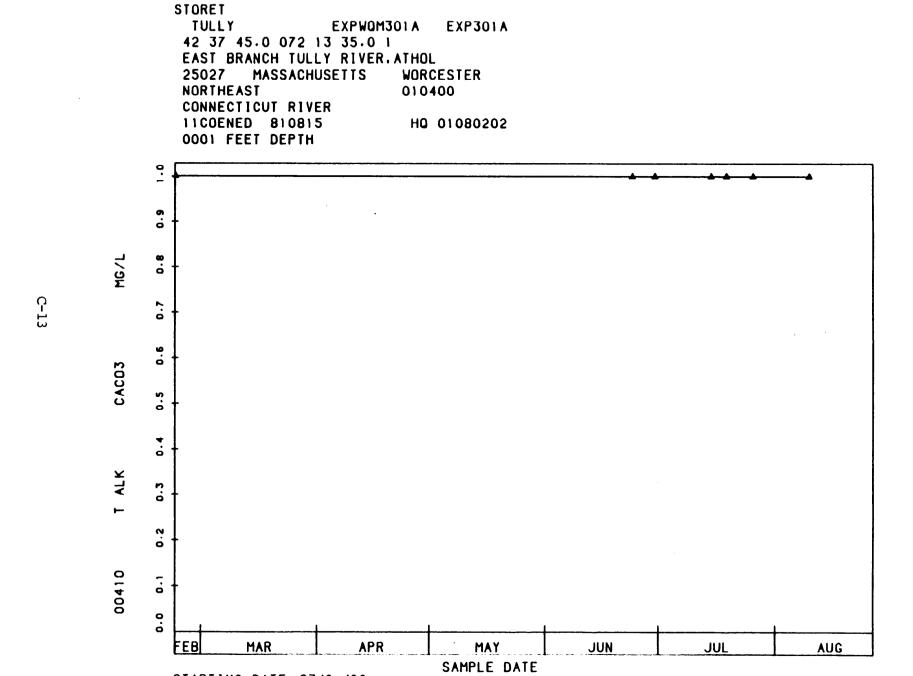
MG/L

CACO3

ALK

00410

STARTING DATE 71/6 /28

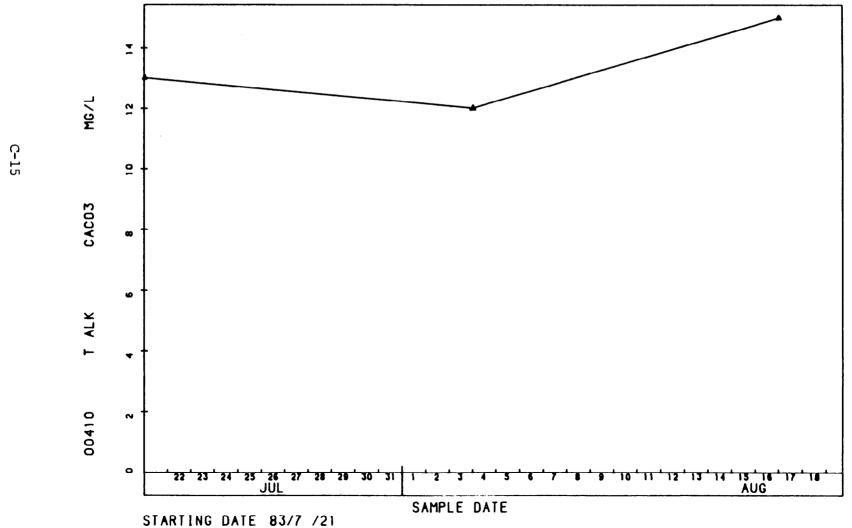


STORET WT03 EXPOUT350 EXP350 41 56 46.0 071 54 05.0 1 QUINEBAUG RIVER BELOW WEST THOMPSON DAM 09015 CONNECTICUT WINDHAM NORTHEAST 010500 THAMES RIVER 11COENED 01100001005 0002.910 ON 0001 FEET DEPTH | 1972 | 1973 | 1974 | 1975 | 1976 | 1977 | 1978 | 1979 | 1980 | 1981 | 1982 | 1983 | 1984 | 1985 | 1986 | 1987 | 1988 | 2 MG/L CAC03 ALK m 0

SAMPLE DATE

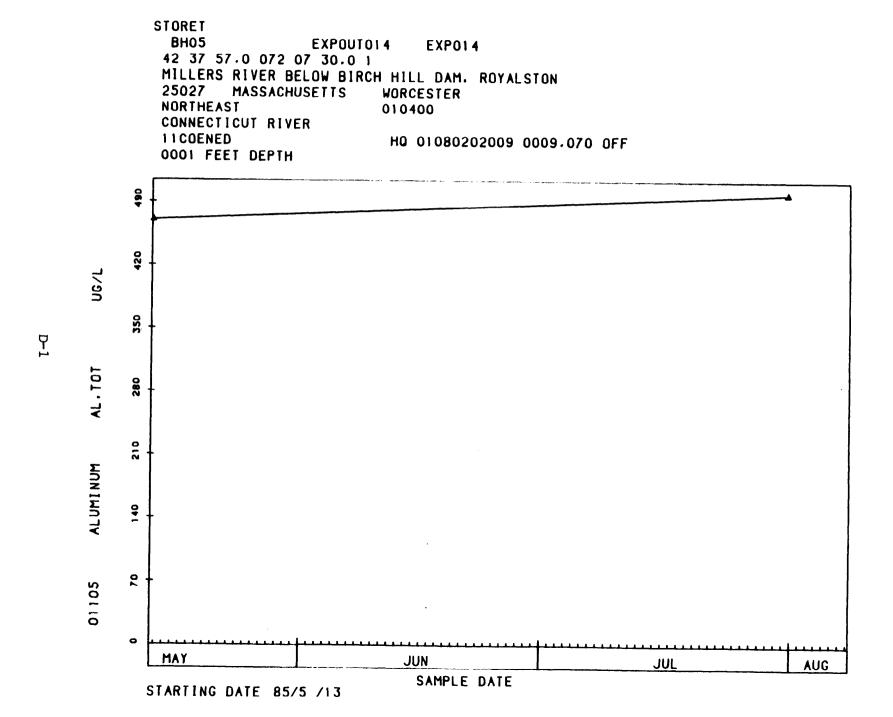
STARTING DATE 71/8 /2

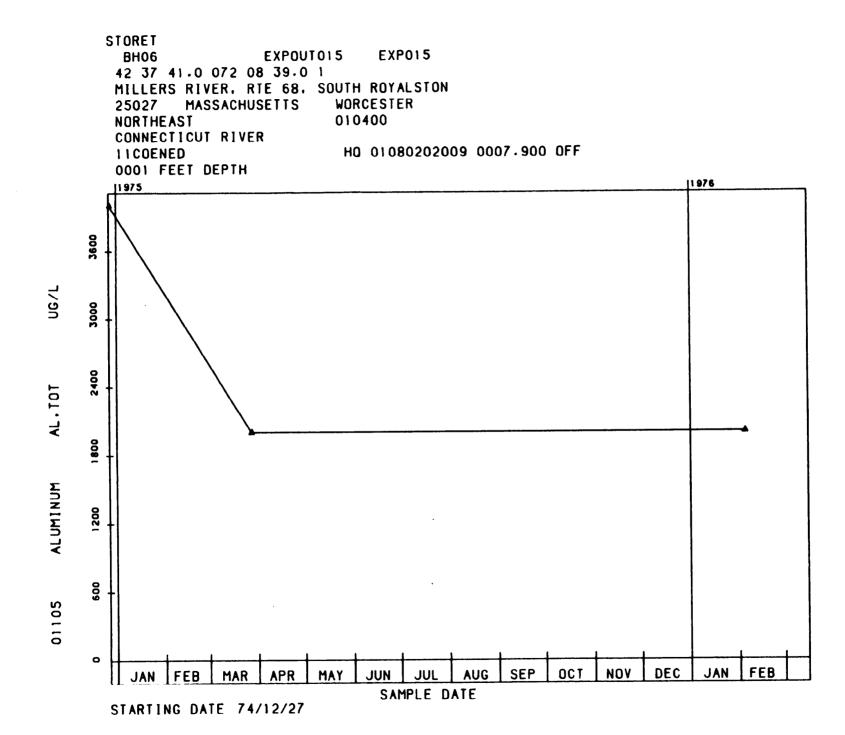
STORET
WTHO EXPWOM347 EXP347
41 56 46.0 071 54 05.0 1
QUINEBAUG RIVER BELOW WEST THOMPSON DAM
09015 CONNECTICUT WINDHAM
NORTHEAST 010500
THAMES RIVER
11COENED 760721 01100001005 0002.910 ON
0001 FEET DEPTH

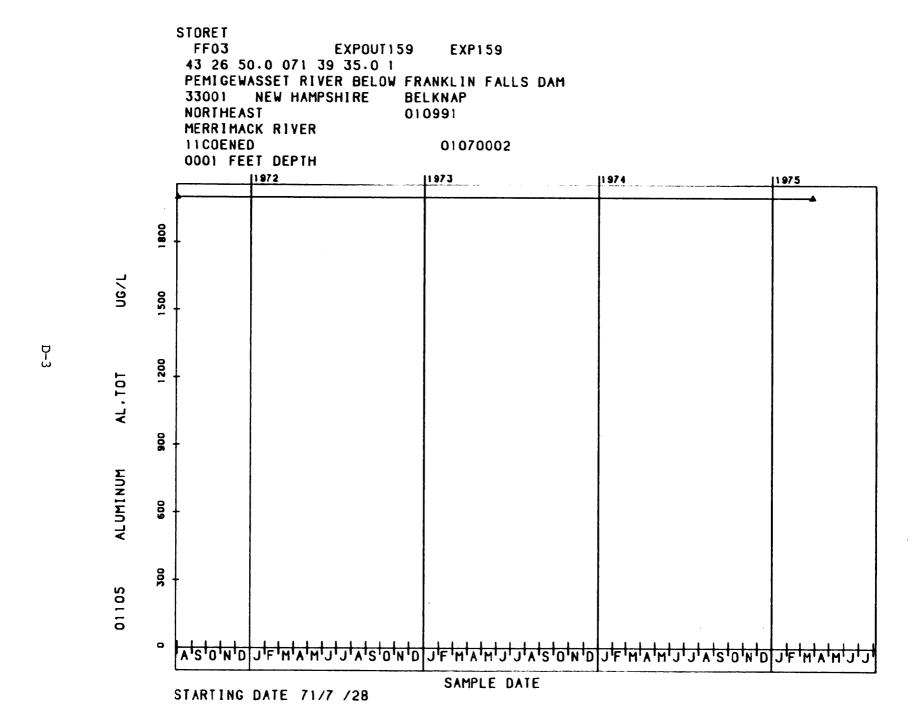


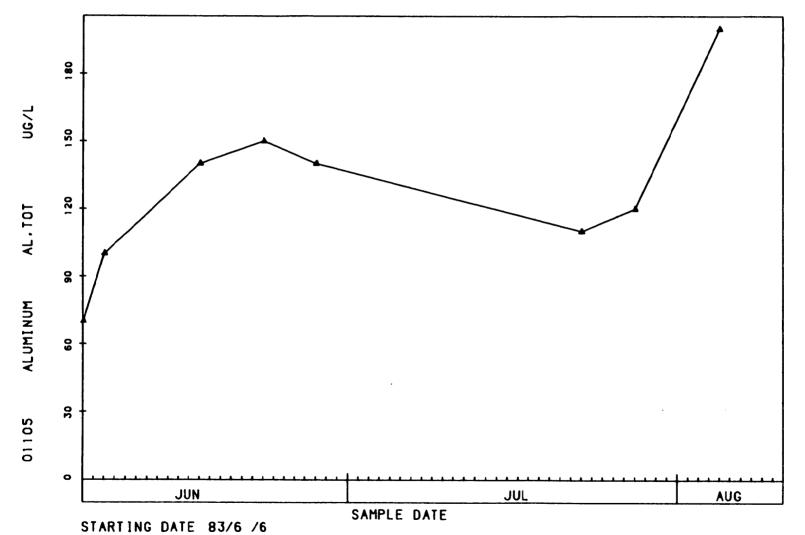
APPENDIX D

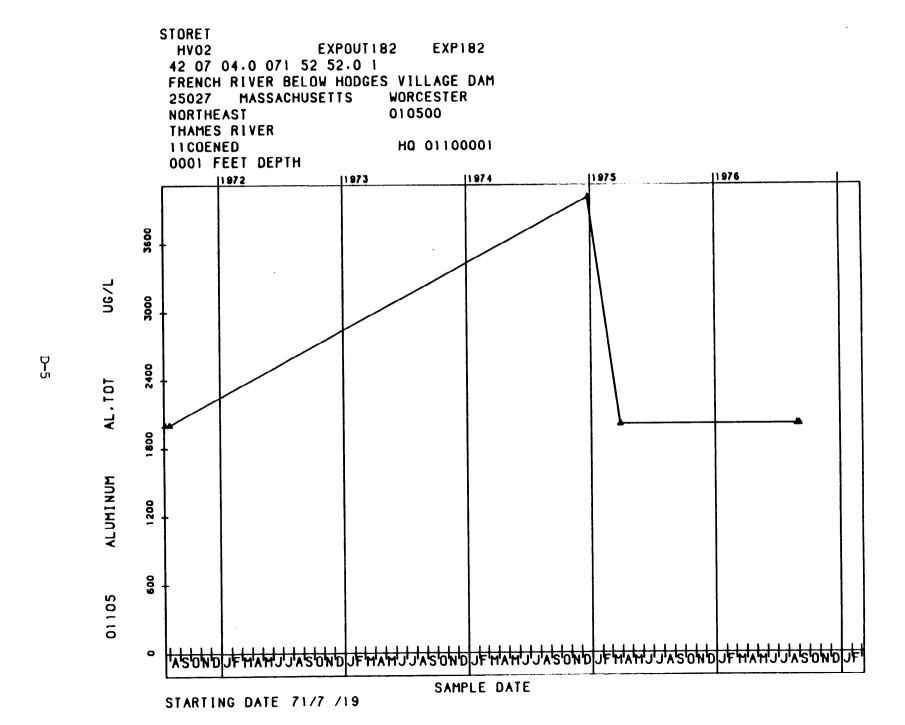
Aluminum Plots







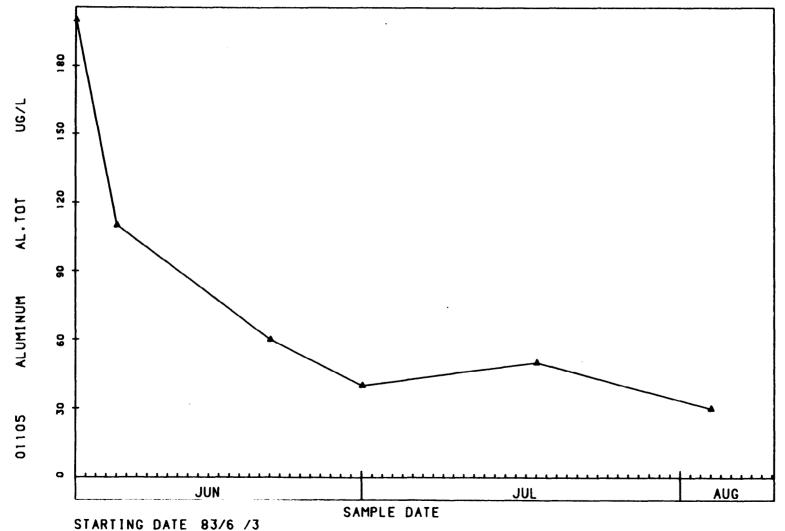




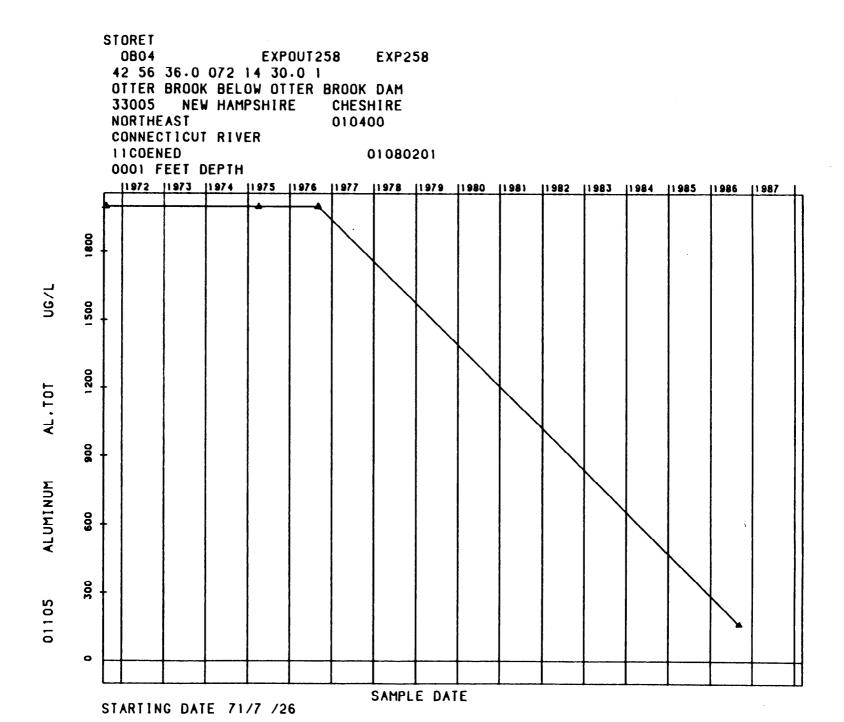
STORET
LITT EXPWOM198 EXP198

42 15 56.0 072 52 50.0 1

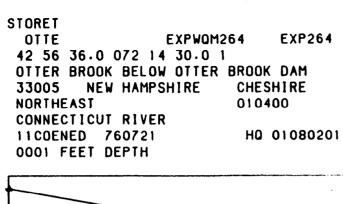
MIDDLE BRANCH WESTFIELD R • LITTLEVILLE DAM
25015 MASSACHUSETTS HAMPSHIRE
NORTHEAST 010491
CONNECTICUT RIVER
11COENED 01080206012 0000.940 ON
0001 FEET DEPTH



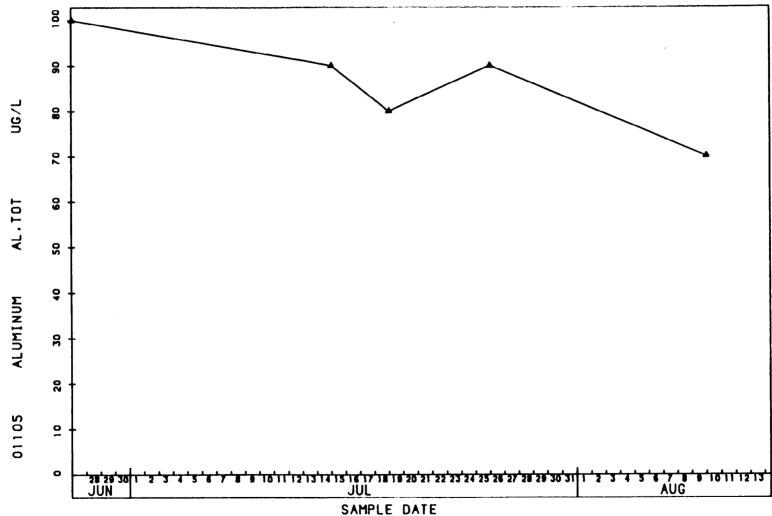




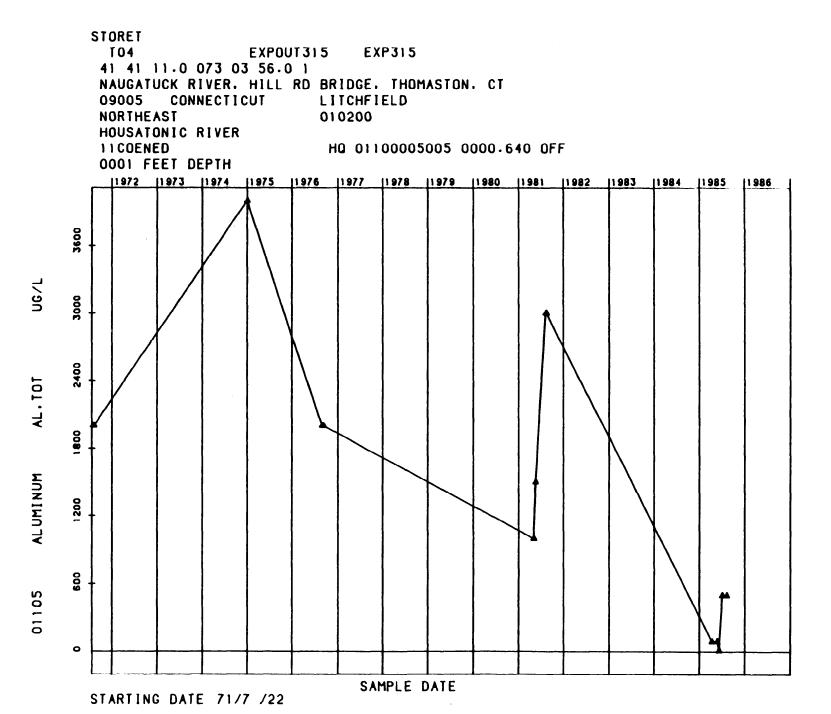


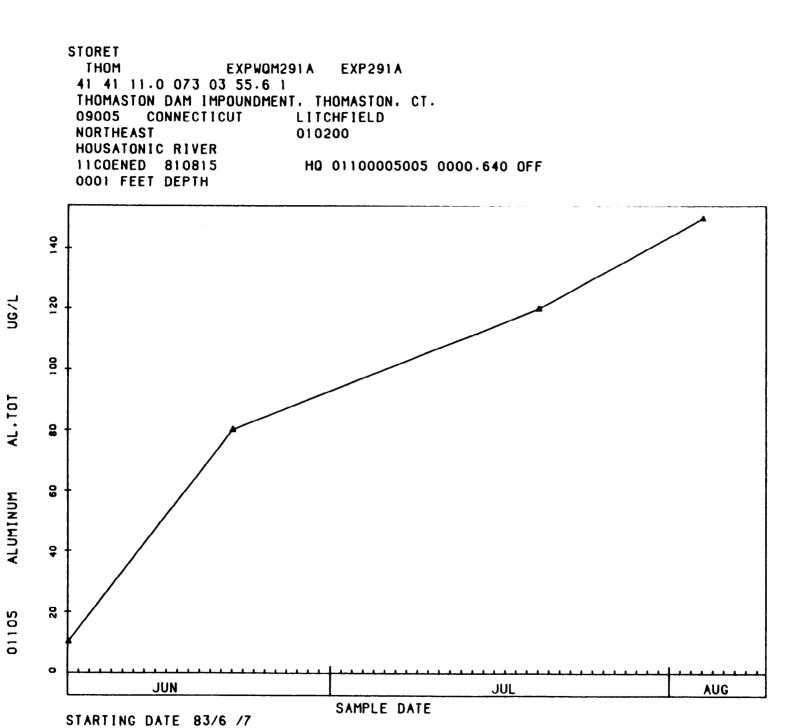


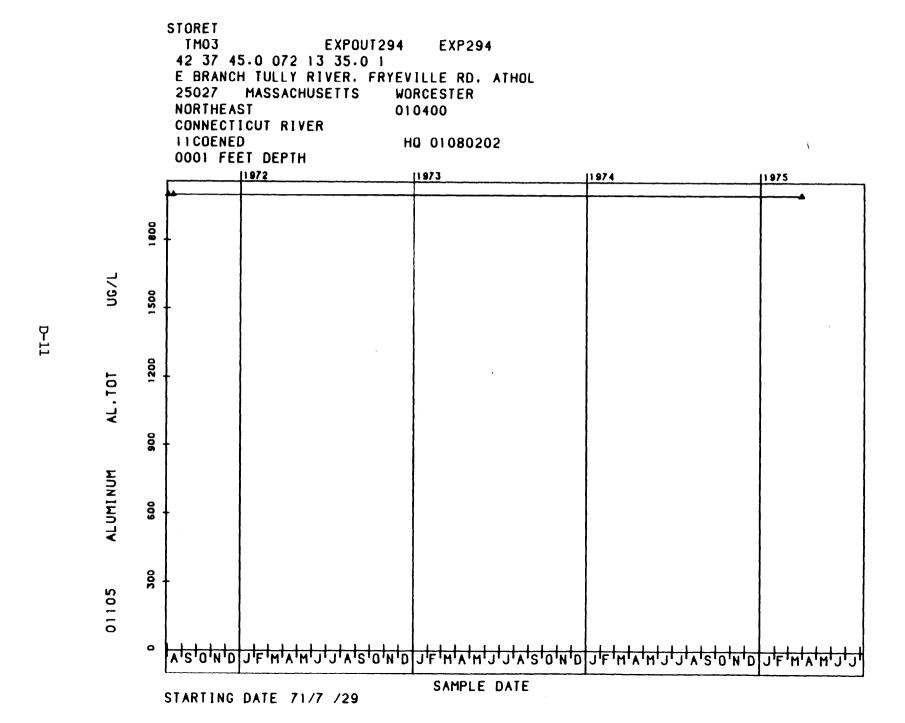
STARTING DATE 83/6 /27

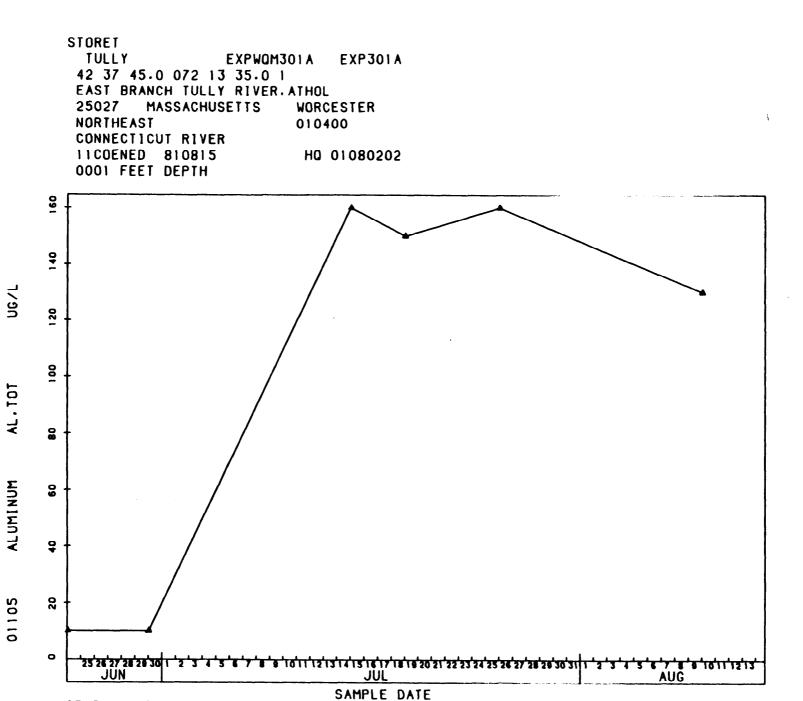








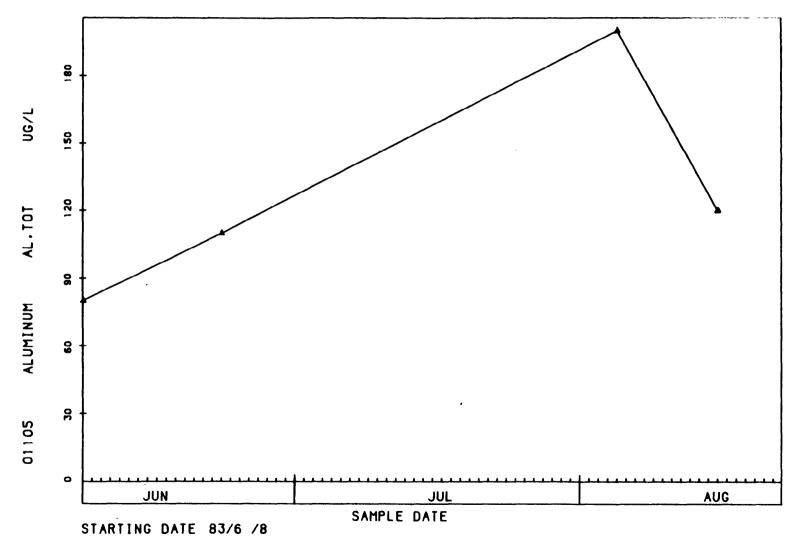




STARTING DATE 83/6 /24

STORET WT03

STORET
WTHO EXPWOM347 EXP347
41 56 46.0 071 54 05.0 1
QUINEBAUG RIVER BELOW WEST THOMPSON DAM
09015 CONNECTICUT WINDHAM
NORTHEAST 010500
THAMES RIVER
11COENED 760721 01100001005 0002.910 ON
0001 FEET DEPTH



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